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ANOMALOUS DIAMAGNETISM OF SELENIUM

By MATA PRASAD and S. S. DHARMATTI

The problem of anomalous diamagnetism was originated by Honda[1] who observed that colloidal bismuth is only about one-third as diamagnetic as the electrolytically prepared metal. Much importance was not attached to this observation until an explanation was put forward for the high diamagnetic susceptibility of bismuth by Ehrenfest[2] and of graphite by Raman[3] on the assumption that there exist in these crystals electron orbits which encircle more than one atom of the lattice. Since then a systematic study of the magnetic properties of metals has been undertaken by a number of workers when these are (*i*) either finely powdered or brought into a colloidal state, (*ii*) cold worked and (*iii*) made up into thin films. As regards the first item important conclusions have been drawn by two schools of workers from their extensive study of a number of colloidalised and finely powdered metals.

On the considerations that Ehrenfest-Raman bindings exist in some metals, and the contribution of these bonds to the diamagnetic susceptibility decreases when the metals are finely powdered, Rao[4] (see Paramasivan[5] and Vaidianathan[6]) studied graphite, bismuth and antimony and determined the particle sizes at which a change in the diamagnetic susceptibilities takes place. The experimental results of these workers have been confirmed by Miwo[7] and by Goetz.[8] Also there is incidental agreement between the critical size of the particles and the sides of the etched figures formed at the surfaces of the crystals of the metals. Rao[9] also observed changes in the susceptibility of metals which do not possess Ehrenfest-Raman bindings on colloidalisation and has explained his observations on the theory of cold working of metals by Honda and Shimizu.[10]

Bhatnagar[11] and collaborators[12] have also studied the magnetic behaviour of a large number of metals, including some of those studied by Rao, and have shown that the changes in the susceptibilities attributed by Rao and other workers to changes in the size of the particles when the metals are colloidalised either by powdering or by arcing are really due to the presence of impurities which can be removed by properly treating the powders with suitable reagents. According

to Bhatnagar the susceptibility of metal can only change when either its crystal structure is altered or it is converted into an allotropic modification during colloidalisation. The entire position regarding the question of the so-called anomalous diamagnetism has been recently surveyed by Lessheim[13] who has concluded that the available experimental evidence supports Bhatnagar's viewpoint and the effect due to the increased surface is far too small to account for the observed decreased diamagnetism.

The authors have studied the effect of powdering and colloidalisation on the magnetic properties of selenium which was selected for investigation because a colloidal solution of the metal can be very easily prepared without introducing any impurities. A note by Dharmatti[14] described that the diamagnetic susceptibility of grey crystals of selenium decreases on powdering the metal in air and after a certain stage of fineness it becomes paramagnetic. Verma and Gupta[15] who used red variety of selenium have also noticed a slight decrease in the diamagnetic susceptibility on powdering the metal under benzene and toluene but the powdered samples regain their original value after washing them with dilute hydrochloric acid.

EXPERIMENTAL AND RESULTS

The susceptibility was measured by a magnetic balance of the Curie-Wilson type and all errors due to the asymmetry and the change in the position of the tube in the balance were avoided. No attempt was made to maintain the temperature constant as the diamagnetic susceptibility is known to undergo no change with temperature. The accuracy of the balance was tested by measuring the susceptibility of standard substances.

Kahlbaum's purest crystals of selenium ($\chi = -0.336 \times 10^{-6}$) were powdered in an agate mortar free from any ferrogeneous materials in air and the susceptibilities of samples obtained after powdering for different intervals were determined from the formula

$$\chi = \frac{1}{M} \left[\chi_a m_a + (\chi_w m_w - \chi_a m_a) \frac{D - D_1}{D_2 - D_1} \right]$$

where the different terms used have the usual meanings. The results obtained (table I) show that the susceptibility decreases as selenium is more and more finely powdered in air. • Previous trials had shown that no effect of powdering is produced in selenium until the crystals have been powdered for 15 hours.

TABLE I.

Period of powdering	$\chi \times 10^6$
15 hours	-0.2887
24 hours	-0.2456
33 hours	-0.1108
40 hours	$+0.0073$
43 hours	$+0.0337$
46 hours	$+0.0862$

During powdering it was observed that the dark grey colour of the metal crystals of selenium changed first to a pink and afterwards to a red colour. It is, therefore, probable that during powdering in air some oxide of selenium may have formed on the surface of the particles of the powder as has been observed in the case of bismuth and antimony. The most stable oxide of selenium is selenium dioxide which is soluble in alcohol. But the observed decrease in the diamagnetic susceptibility of selenium cannot be due to its presence in the powders as the purest selenium dioxide obtained from Kahlbaum was found to have the diamagnetic susceptibility, 0.3855×10^{-6}, higher than the susceptibility of the metal selenium. However, on the consideration that other oxides of selenium which may have formed during powdering in air are soluble in alcohol, the powders were washed with absolute alcohol, dried thoroughly in a vacuum desiccator and their susceptibilities were determined. It was found that this treatment increased the diamagnetic susceptibility only very slightly but in no case the mass value of selenium was reached nor the paramagnetic powders became diamagnetic. These results lead to the conclusion that the impurities (possibly some complex oxides) present in selenium powders are not readily soluble in alcohol.

In order to eliminate the effects due to the adsorption of gases from the atmosphere during powdering, selenium was powdered under paraffin. The samples were taken out at different intervals, washed with ether and then with alcohol and were dried in a vacuum desiccator over phosphorous pentoxide. The susceptibility of the powders measured immediately after drying indicated that the diamagnetic susceptibility of selenium decreases even when selenium is powdered under paraffin but when the powders were allowed to stand for some time the results given in the following table were obtained :—

TABLE II.

Period of powdering	Size of the particle	$\chi = 10^{-6}$
5·5 hours	...	−0·3252
18 ,,	2·4 μ	−0·2386
26 ,,	1·6 μ	−0·2356

The size of the particles given in the above table was determined by placing a few drops of the suspension of the powder in propyl alcohol in the cavity of a glass slide and measuring the diameters of at least 25 particles along three perpendicular directions by means of a scale provided in the high power microscope.

SELENIUM SOL.

A sol. of selenium was prepared in the following manner. Selenium was dissolved in Merck's pure carbon disulphide (solvent in which selenium is readily soluble) and solution was added to Merck's pure ether (solvent in which selenium is insoluble). A beautiful red coloured sol. thus obtained was evaporated to dryness in air and the susceptibility of the red-coloured coagulum was measured. It will be seen that in this method of preparing the sol. no addition of electrolytes is necessary for causing the coagulation of the colloidal particles. In order to ascertain the action of air on the particles a second sample of the sol. was prepared which was dried in vacuum. The results obtained with the two samples are given in the following table:—

TABLE III.

	Sol. in air	Sol. in vacuum
$\chi \times 10^6$	+0·0188	−0·2246

EFFECT OF HYDROCHLORIC ACID

To examine the effect of treating the selenium powders with hydrochloric acid. Some of the powders were sent to Verma and the results obtained by them have been reported by Verma and Gupta (*loc. cit.*) and are as follows:—

TABLE IV.

$$\chi \times 10^{-6}$$

Before washing	After washing
$+0.228$	-0.307
-0.135	-0.301

One of the powders washed by the authors gave a highest value -0.2224×10^{-6}. In all cases it was observed that the red colour of the powders was not altered by the treatment with the acid.

These results can be explained on the consideration that during powdering and colloidalisation selenium is converted into an allotropic modification. This assumpation is justified as (i) the colour of the original selenium is grey and that of the powder or colloidal selenium is red and (ii) the susceptibility of the purified sample does not change to its original value when either the powdered or colloidalised sample is melted.

The change in the susceptibility due to the passage of selenium into an allotropic modification can be theoretically calculated from Honda and Shimizu's[16] theory, which has been successfully applied by them to the conversion of tin, copper, silver and gold into allotropic modifications on melting. These authors assume that the susceptibility is affected by the volume change caused by an allotropic change in two ways:

1. The change of paramagnetic susceptibility due to the diminution of free electrons caused by the expansion, and this is given by, according to Pauli, Landau and Posener[17]

$$d\chi_1 = +\frac{2}{9} \frac{CL^{1/3}a^{1/3}}{W^{1/3}p_0^{2/3}} \left\{ -2 + \frac{A}{3a_0} \left(\frac{4\pi}{3M} p_0 \right)^{0.488} \right\} \frac{dp}{p_0}$$

Where $C = 2.21 \times 10^{-14}$, $L =$ Loschmidt's number per mol, $W =$ atomic weight, $\rho =$ density, $a =$ number of free electrons per atom.

$A = 2.261 \times 10^{-12} Z^{0.513}$, $Z =$ the atomic number and $M =$ mass of the atom.

2. The change of diamagnetic susceptibility due to the increase of bound electrons caused by the expansion and is given by, according to Sommerfeld and

Hironé

$$dx_2 = -\frac{4\cdot13\times10^{-7}Z^{-\frac{2}{3}}a_0x_0}{aW} \left(\frac{3M}{4\pi}\right)^{\frac{1}{3}}\rho^{-\frac{1}{3}} \frac{d\rho}{\rho_0}$$

$$+ \left\{ 2\cdot06\times10^{-7}\times x_0{}^2 Z^{-\frac{2}{3}} + 0\cdot662\times10^{-5}a_0{}^{-2/3} \right\} \times$$

$$\frac{A}{W}\left(\frac{4\pi}{3M}\rho_0\right)^{0\cdot488}\frac{d\rho}{\rho_0}$$

where the various terms have the same meaning as given by Honda and Shimizu (*loc. cit.*), *viz.*,

$$x = \frac{r}{a}, a = \frac{0\cdot4676}{Z^{1/3}}\times 10,^{-8} r = \left(\frac{3M}{4\pi\rho}\right)^{1/3}.$$

Honda and Shimizu point out that in the case of contraction the changes due to 1 and 2 are exactly opposite. In the latter case if the original metal is diamagnetic, the allotropic modification will be less diamagnetic, as observed in the present case.

The density of grey selenium is 4·19. A search through the literature shows that there are two varieties of red selenium, crystalline and amorphous. The density of the crystalline red selenium, taken as the mean of several observers is 4·50 and that of the amorphous one, is 4·26 (*cf.* table V).

TABLE V.

Amorphous red.		Crystalline red	
Schaffgotsch	4·245—4·275	Critical Tables	4·5
Rammelsberg	4·27—4·34	Partington	4·47
Cholodny	4.28	Mitscherlich	4·46—4·509
Rathke	4·26—4·28	Peterson	4·46
Saunders	4·26	Cholodny	4·44
Partington	4·26	Saunders	4·44—4·47
Cholodny		C. F. Rammelsberg	4.51
(colloidal red)	4·26	E. Peterson	4·63

(*Cf.* Mellor, p. 712, Vol. X.)

The value of a_o required for above calculations has been determined, as suggested by Honda and co-workers, [17] from the graph in which the values of a_o determined by these workers for various metals is plotted against the atomic weights of the metals and is found to be o·066. The results of calculations are given in the following table:—

TABLE VI

$$a_o = \text{o·066}, \qquad \rho = 4\text{·19}$$

Phase change	red crystalline	red amorphous
$\dfrac{d\rho}{\rho_0}$	+ o·0734	+ o·016
$d\chi_1$	+ o·0129 × 10⁻⁶	+ o·0029 × 10⁻⁶
$d\chi_2$	+ o·1106 × 10⁻⁶	+ o·025 × 10⁻⁶
$d\chi$	+ o·1235 × 10⁻⁶	+ o·028 × 10⁻⁶
χ(theor.)	− o·2125 × ⁻⁶*	− o·308 × 10⁻⁶**
χ(obs.)	− o·2224 × ⁻⁶	− o·306 × 10⁻⁶

*$\chi \times 10^6 = -\text{o·336} + \text{o·1235} = -\text{o·2125}$ *$\chi \times 10^6 = -\text{o·336} + \text{o·028} = -\text{o·308}.$

The calculated value for the red amorphous variety of selenium agrees admirably with the value obtained after washing the selenium powders with hydrochloric acid and leads to the conclusion that these powders are red amorphous selenium. The value calculated for the red crystalline form of selenium is within 5 per cent. of the values obtained for (1) the selenium sol, (2) one of the powders after washing with hydrochloric acid and (3) the powders obtained by grinding selenium under paraffin. This agreement between the calculated and the observed results may lead to the conclusion that the above mentioned powders of selenium are crystalline.

Ashara[18] has shown that crystalline graphite when coiloidalised for a number of days gives a broad diffuse ring in the x-ray diffraction photograph. Hence evidence for the crystalline nature of the red selenium is being collected from an x-ray examination of these colloidalised powders. At present it is hard to define the conditions which govern the formation of the amorphous and crystalline red varieties of selenium on powdering and colloidalisation. From the results obtained so far it is clear that a large amount of the change in the susceptibility of the grey selenium on powdering and colloidalisation in air is due

to some impurities which are removed by treating the powders with hydrochloric acid. The rest of the change is due to the conversion of the grey selenium into an allotropic modification which is red in colour and may either be crystalline or amorphous or a mixture of the two.

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INVESTIGATIONS IN THE INFRA-RED

Part II.

Absorption Spectrum of Boric Acid.

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ABSTRACT. The infra-red spectrum of boric acid, H_3BO_3 has been investigated between the region 5μ to 15μ. As many as eight absorption bands have been observed. Three of them correspond to the vibrational frequencies associated with the BO_3 radical while the others are due to the molecule $B(OH)_3$.

INTRODUCTION.

In a previous communication [1] the molecular structure of inorganic borates as revealed from the study of their near infra-red absorption spectra was discussed. The radical BO_3 was assigned a plane triangular configuration, having three active vibrational frequencies corresponding to the bands at $7·5\mu$, 11μ and 14μ and an optically inactive one at 9μ. The magnitude of the latter was, however, postulated from an analogy with the radicals CO_3 and NO_3. It was proposed there to ascertain correctly this inactive frequency from a study of the Raman spectra of these salts.

Meanwhile Joglekar and Thatte [2] have investigated the Raman spectra of a few organic and inorganic borates. In addition to the fundamental frequency at 14μ, they have identified a Raman frequency corresponding to the optically inactive one at 9μ as assumed above for the BO_3 radical. Very recently the results of the above authors on organic borates have been in main confirmed by Ananthakrishnan [3] who has also studied the Raman spectrum of boric acid. A continuous background rendered it difficult to identify more than one Raman frequency at 875 cm^{-1} which he attributed to the H_3BO_3 molecule. It was therefore thought desirable to investigate the infra-red spectrum of this molecule where the above difficulty can be avoided and thus obtain more complete data of its vibration frequencies which may lead to an understanding of its constitution.

EXPERIMENTAL RESULTS.

The experimental arrangement and the region of investigation are same as in previous work. Fig. 1 shows the absorption curve for boric acid. The wave-

lengths of the characteristic bands and the corresponding frequencies are tabulated in table I. For comparison, the Raman frequency data of methyl borate between the region $5\mu - 15\mu$, as well as the infra-red data of inorganic borates are included.
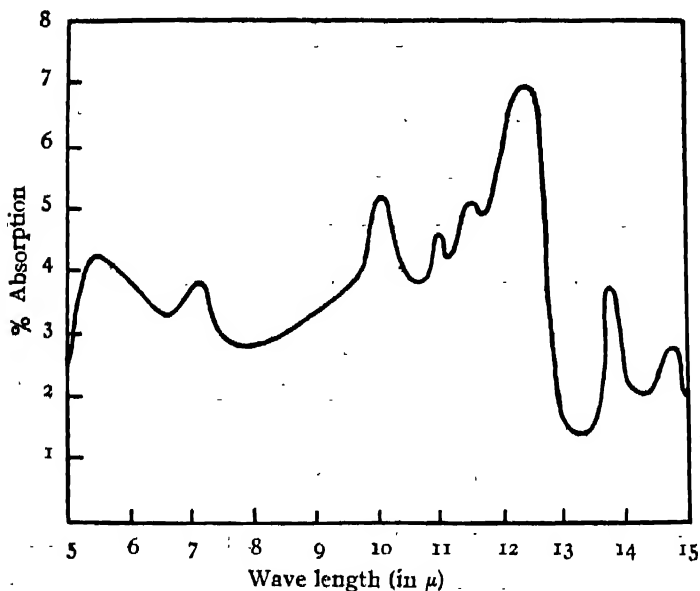
FIGURE I.

TABLE I.

Infra-red data.		Raman Spectra data.		
Boric Acid (H$_3$BO$_3$).	Inorganic Borates -(BO$_3$).	Methyl Borate (CH$_3$)$_3$BO$_3$.		Boric Acid H$_3$BO$_3$.
Author.	Sen and Sen Gupta.	Ananthakrishnan.	Joglekar and Thatte.	Ananthakrishnan.
675 (14·8μ)				
724 (13·8μ)	715 (14·0μ)	728	710	
800 (12·5μ)				
869 (11·5μ)			860	875
909 (11·0μ)	909 (11·0μ)			
990 (10·1μ)				
		1030	1028	
		1117	1112	
		1174		
1389 (7·2μ)	1333 (7·5μ)			
		1460	1459	
			1563	
			1753	
1818 (5·5μ)				
			1959	

INTERPRETATION OF RESULTS.

It is evident that the three active frequencies corresponding to $7.5\ \mu$, $11\ \mu$ and $14\ \mu$ which have been previously attributed to the BO_3 radical from a study of the infra-red absorption spectra of the inorganic borates are also present in the spectrum of boric acid. Similar relationship has been noticed between dilute nitric acid and inorganic nitrates. Dadieu and Kohlrausch [4] observed that although the Raman spectra of conc. HNO_3 and organic nitrate CH_3ONO_2 are very similar, the spectrum of the diluted acid resembles that of its inorganic salts. This behaviour has been attributed to the dissociation of HNO_3 into H and NO_3 ions on dilution. Recently Aderhold and Weiss [5] also have come to the same conclusion. In the case of sulphuric acid Woodward [6] and others [7] are of opinion from the study of its Raman spectrum that with dilution the molecule first dissociates into HSO_4' and then into SO_4'' ions.

The frequencies 675, 869 and 990 cm^{-1} may be attributed to the molecule, H_3BO_3. Of these, the one at 869 cm^{-1} is evidently identical with the Raman frequency, 875 cm^{-1}, reported by Ananthakrishnan and assigned to the totally symmetrical vibration of the molecule $B(OH)_3$. The justification of attributing the two frequencies, 675 and 990 cm^{-1}, to H_3BO_3, is derived from a comparison of their magnitudes with those of the Raman frequencies observed in the spectra of H_3PO_3 by Ghosh and Das.[8] For the latter molecule, these authors have reported three frequencies at 672, 940 and 1012 cm^{-1}. The first two seem likely to correspond to the frequencies 675 and 990 cm^{-1} observed in the infra-red spectrum of boric acid. It may, however, be mentioned that corresponding to the frequency at 1012 cm^{-1}, a Raman frequency of magnitude nearly 1028 cm^{-1} has been observed in the spectrum of methyl borate. This does not appear in the infra-red spectrum of boric acid and is probably an optically inactive frequency.

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A RAY-DISPLACEMENT REFRACTOMETER
FOR ACCURATE WORK

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ABSTRACT. The paper describes a very convenient and accurate type of refractometer, which can be built up in any Physical laboratory without much trouble. The probable error of the mean value of μ determined by this apparatus is found to be $\pm$ ˙0002 and possesses a high degree of reproducibility.

It is specially suited for the determination of μ of thin transparent plates obtainable in small sizes, but can also be used for liquids.

§ 1. INTRODUCTION AND THEORY.

In a paper read before the Indian Science Congress at Patna in 1933, and published elsewhere,[1] it was shown that by using the equations

$$d = \frac{t \sin (i - r)}{\cos r} \qquad \ldots \quad (1)$$

and

$$\mu = \frac{\sin i}{\sin r}, \qquad \ldots \quad (2)$$

the refractive index of a plate of thickness t on which a ray of light is incident at an angle i, producing a lateral shift of magnitude d, can be calculated with the help of the following equation obtained by eliminating r between the above two equations, namely

$$\mu = \frac{\sin i}{t \sin i - d} \sqrt{d^2 + t^2 - 2d \cdot t \cdot \sin i} \qquad \ldots \quad (3)$$

Figure 1 shows the incident and the displaced path of a ray.
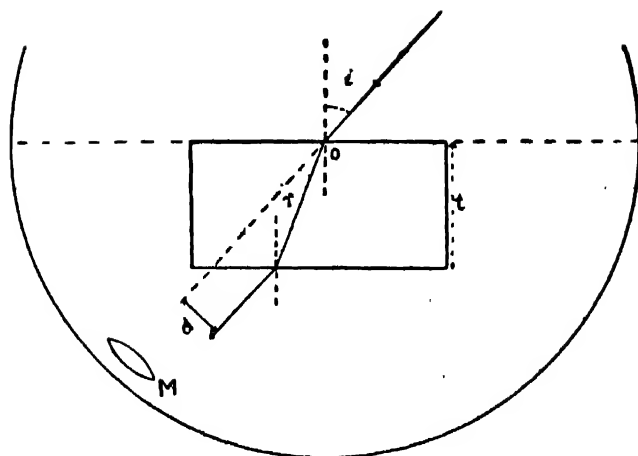
FIGURE I.

In that paper, measurements of refractive indices of ordinary thin glass and fused quartz plates with respect to sodium light were given. The experimental plate was mounted on a rod fixed along the horizontal axis of rotation of a theodolite whose circular scale and vernier enabled the angles of incidence to be determined. A microscope focussed on a sharp dark line was used to measure its displacement whenever the experimental plate was interposed between the index line and the objective of the microscope so that the angle of incidence was other than zero. It was also stated in that paper that, the method could be further improved both in the direction of higher accuracy of result as well as for the determination of dispersion of the refracting plates. It is the purpose of this paper to describe an experimental arrangement by which refractive indices of thin plates can be determined very conveniently with respect to any wave length of light with an accuracy comparable with that of some of the standard methods known at present.

§ 2. APPiARATUS AND ADJUSTMENTS.

The apparatus consists of a spectrometer in which the telescope is replaced by a microscope having scale divisions in the eyepiece.

A Hilger constant deviation spectroscope is used as a monochromator in place of the collimator of the spectrometer. The whole assembled apparatus is shown in plate I, figure 2.

(I) The microscope is focussed on a silk fibre carrying a small plumb placed as nearly as possible on the axis of rotation of the prism table of the spectrometer. A fine line normal to the direction of the light from the monochromator to the microscope is drawn on the prism table passing through the axis of rotation.

(II) The slit of the monochromator is illuminated by sodium light and the drum rotated so that the slit image is in focus exactly on the centre division mark of the eyepiece scale of the microscope.

(III) The experimental plate, if thin, is attached with a little wax to a rectangular metal base piece so that one of its faces, when placed on the prism table contains the axis of rotation. Care is taken to see that the plate is vertical. This face of the plate faces the monochromator. The line drawn on the prism table helps this adjustment.

(IV) Generally, as soon as the refracting plate is put in position on the prism table, the slit image as seen in the microscope will shift from the original position at the centre of the scale. This shift indicates that the light is not falling normally on the plate.

The prism table is then slowly rotated so that the slit image comes back to its former position at the centre of the eyepiece scale. When this is secured the angle of incidence is zero on the plate. The reading of the vernier attached to the prism table is then recorded. The mean of several independent settings is taken as giving the correct position of the material for normal incidence.

Now the prism table is rotated so that the slit image shifts a complete number of the eyepiece scale divisions. The vernier is again read and the difference of the two readings gives the angle of incidence of light on the refracting plate. In actual practice shifts of equal amount on both sides of the initial zero of the eyepiece were produced, involving a change in the angle of rotation by $2i$; from this, i was determined.

The scale divisions of the eyepiece having been calibrated before in cms., the thickness of the experimental plate being known from measurements with a spherometer or some other instrument, all the quantities from which the refractive index of the plate can be determined according to the formula (3) become known, and hence μ is calculated. Similar procedure is followed with respect to any other line of the spectrum which merely a rotation of the monochromator drum brings in the desired position.

§ 3. SOURCES OF LIGHT AND OTHER EXPERIMENTAL DETAILS.

The slit of the monochromator is kept sufficiently wide to give images of sufficient intensity in the focal plane of the observing microscope. The setting can be made on one of the sharp edges of the illuminated slit image, but it was

found a distinct advantage, in practice, if a very fine silk fibre be stretched verti-cally along the monochromator slit at its middle, and the setting be made with respect to the fine dark shadow of this fibre against the scale division marks of the microscope.

The best sources of light that could be recommended for use are the Geissler tubes or metallic vapour tubes run with an induction coil or a small transformer. Any source in which the luminous vapour flickers, such as an arc, is not suitable for the apparatus, inasmuch as the flickering and the roving of the luminous mass shift the position of the shadow of the silk fibre in the field of view and make accurate setting a matter of some uncertainty. The Geissler tubes on the other hand, have been found in practice to be extremely steady and satisfactory in their behaviour and no shifting of the fibre shadow is at all noticeable.

The spectrometer used in these experiments was supplied by Messrs. Bellingham and Stanley and has a very massive and steady base. The graduated circle a radius of 15 cms., a degree is divided into four divisions in the main scale and the least count is 20'' (seconds). The microscope used had a magnifying power 50.

The apparatus is equally suitable for the determination of refractive indices of liquids. For this purpose, a glass cell is used. The first thing is to determine the refractive indices of the glass walls of the cell with respect to the wave lengths desired to be used for any liquid. This is easily done with the help of the equation (3).

The liquid is now poured in the cell and the combined displacements due to the liquid and glass walls of the cell corresponding to, say, 25 divisions of the eyepiece scale, is produced by making the necessary angle of incidence i, say. For this angle of incidence, using the value of the refractive index for glass for any of the light sources, the displacements due to glass alone is calculated using equation (3) again.

From the total displacement produced, the displacement due to the glass walls of the cell alone is now subtracted. The difference is the displacement due to the liquid alone of thickness corresponding to the distance between the inner faces of the cell walls. This distance is previously determined by careful measurements with a microscope. Knowing i and the displacement due to the liquid alone of a known thickness, the refractive index of the liquid is calculated with the help of equation (3).
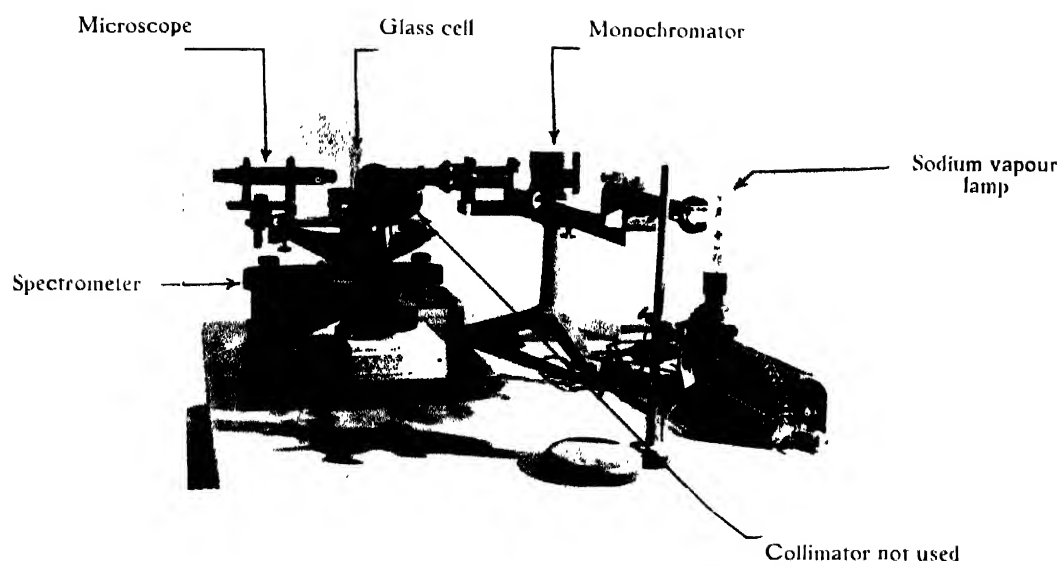
Figure 2.

Measurement of μ for Glass with Sodium Light.

TABLE I.

First sample of glass :—

	Reading of First position.	Reading of Second position.	Difference .. t	i	Displacement	Ref. Index (μ)
1	191°36'40"	141°50'40"	49°46'00"	24°53'00"	·303 mm.	1·5247
2	191°31'20"	141°42'00"	49°47'20"	24°54'40"	,,	1·5237
3	191°28'20"	141°46'00"	49°42'20"	24°51'10"	,,	1·5257
4	191°35'40"	141°45'20"	49°50'20"	24°55'10"	,	1·5233
5	191°33'00"	141°43'40"	49°49'20"	24°54'40"	,,	1.5237
6	191°28'20°	141°41'00"	49°47'20"	24°53'40"	,,	1.5243
7	191°20'20"	141°36'00"	49°44'20°	24°52'10"	,,	1.5253
8	191°16'40"	141°34'40"	49°42'00"	24°51'00"	,,	1·5261
9	191°17'40"	141°31'40"	49°46'00"	24°53'00"	,,	1.5247
10	191°17'00"	141°33'40"	49°43'20"	24°51'40"	,,	1·5256

Mean value of $\mu = 1\cdot5247$.

Probable error of the result $= \pm\cdot0002$.

Second sample of glass :—

The following values of μ were determined on dismantling and reassembling the apparatus (Na light),

(1) 1·5162. (2) 1·5163 (3) 1·5197 (4) 1·5186 (5) 1·5177

(6) 1·5183. (7) 1·5177 (8) 1·5169 (9) 1·5177 (10) 1·5169

Mean value of $\mu = 1\cdot5176$

Probable error of the result $= \pm\cdot0002$.

3

Measurement of Dispersion of some Substances.

<div align="center">

TABLE II.

</div>

Calculated value = A ;

Value reduced to the temperature given in constant book = B ;

Value from the constant book = C.

Substance.	Refractive Indices.			Remarks.
	$\lambda 6563$	$\lambda 5893$	$\lambda 4861$	
Water.	1·3277 at 30°·8	1·3321 at 33°·oC	1·3350 at 30°·8C	A
	1·3278 at 30°·oC	1·3325 at 30°·oC	1·3351 at 30°·oC	B
	1·3302 at 30°·oC	1·3320 at 30°·oC	1·3360 at 30°·oC	C
Toluene.	1·4894 at 29°·8C	1·4946 at 29°·8C	1·5035 at 29°·8C	A
		1·49457 at 30°·oC		B
		1·4918 at 30°·oC		C
Ethyl benzene.	1·4801 at 31°·oC	1·4866 at 31°·oC	1·4972 at 31°·oC	A
		1·4920 at 20°·oC		B
		1·4966 at 20°·oC		C
Benzene.	1·4806 at 31°·8C	1·4936 at 31°·8C	1·5006 at 31°·8C	A
		1·4974 at 25°·oC		B
		1·4979 at 25°·oC		C
Glass.	1·5106	1·5135	1·5198	μ of the material of the cell used.
Quartz (Right handed)	1·5450	1·5499	1·5530	
Didymium glass.	1·5182	1·5222	1·5280	

<div align="center">

§ 4. ACCURACY ATTAINABLE WITH THE APPARATUS
AND ITS ADVANTAGES.

</div>

In the earlier paper (*loc. cit.*) some of the important methods for the accurate determination of refractive indices of thin transparent plates of solids had been

summarised. The results of measurements on glass by successive settings given in table I, show that the probable error of the mean result is $\pm \cdot 0002$ and that a dismantling of the whole arrangement and reassemblage do not change the probable error. This means that the apparatus can be relied upon for reproducing results within the same degree of accuracy.

It is interesting to compare the degree of accuracy obtained with this form of refractometer with that which some other well known apparatus possess. The latter is listed in Handbuch der Physik, Band XVIII, 1927, pp. 643, 700, 702, 687, from which it would appear that the uncertainty lies in the fourth decimal place in most cases and this is what is claimed for this apparatus.

A very much higher degree of accuracy has been claimed for the Jamin and the Rayleigh forms of the refractometer, but the strict temperature control necessary to be able in reality to utilise the full power of the instruments with reliability, is a matter of such practical difficulty as to be well nigh impossible of realisation in the majority of cases.

Table II contains results of measurements of refractive indices of a number of liquids and solids with respect to three standard lines, namely the red H_α, green H_β lines of hydrogen, and the yellow line of sodium. These values enable the dispersion of the materials to be easily calculated.

The observed values of refractive indices at the temperature of the experiment have been reduced to the values at temperatures given in the Constant books with the help of appropriate co-efficients when available in the books, for the lines chosen. The best agreements in the case of liquids is to be found for water and benzene for sodium light where the accuracy lies in the fourth decimal place. These were the purest liquids we had. The results with respect to H_α line are not so accurate because of the difficulty of visual observation in that region.

It will thus be seen, that the results obtained with this form of refractometer whose chief merit lies in being inexpensive and capable of being built up of parts easily obtainable in any physical laboratory, are of considerable degree of dependable accuracy.

Further, the instrument to be used requires only a small bit of a plane parallel transparent plate and does not require the substance to be cut in any particular form and thus possesses an advantage of its own.

It is intended to describe the application of this new type of refractometer to the study of the anomalous dispersion of didymium glass, in a subsequent paper.

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REFERENCE.

1 P. S. C. Bulletin No. **3**, p. 24, 1933.

STRUCTURE OF AROMATIC COMPOUNDS.

Part I, Acenaphthene.

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ABSTRACT.—From an analysis of the estimated intensities of X-ray reflections from a number of planes and by combining the available magnetic data, it is found that the two fold axis of the molecule lies parallel to the b-axis while the molecular plane is inclined at 26° to the c-face. The estimated intensities are satisfied by the assumption of a plane structure of the molecule. The distance between an aliphatic carbon atom and its adjacent aromatic carbon atoms is 1.47Å°, and that between the two aliphatic carbon atoms is 2.01Å°. The angle between the aliphatic bond and the aliphatic-aromatic bond is 97° and angles between the latter bond and the adjacent bonds in the naphthalene nucleus are 114° and 126°.

INTRODUCTION.

The high rigidity of the benzene ring in aromatic compounds is a very useful guide in the complete determination of the structures of such substances. These rings may be considered as separate units. Their size and shape as well as the arrangements of the carbon atoms inside them are known completely from the determinations of Lonsdale[1] and have been shown to remain unchanged in the condensed rings of naphthalene and anthracene[2] as well by one of the present authors. The benzene ring has been found to occur with its characteristic shape and size in all the aromatic crystals studied later on except in benzoquinone[3] in which the valency bonds inside the benzene ring are altered due to substitution of hydrogen by divalent oxygen. For determining the structures of the more complicated aromatic compounds, it is therefore possible to start with the known structure of the benzene nucleus and thereby the problem is simplified considerably.

Another very important guide to the structures of aromatic crystals is the magnetic property. From experiments on optical scattering and magnetic birefringence it was known that the benzene molecule has a very high optical

as well as magnetic anisotropy. One of the present authors found [2] that the optical and magnetic anisotropies in naphthalene and anthracene crystals measured by Bhagavantam[4] conform nicely with the structures determined from X-ray measurements. This magnetic method was found by Krishnan and his collaborators [5] to be extremely helpful in structure analysis of aromatic compounds. In a series of communications we propose to publish the results of a systematic study of the structures of aromatic organic compounds in which the data of our X-ray measurements are combined with the magnetic properties of the crystals as measured by Krishnan and others or by ourselves, and thereby to determine their atomic arrangements.

In this paper we shall present the results of structure analysis of acenaphthene. The carbon skeleton in the structural formula usually put forward by chemists is given below.
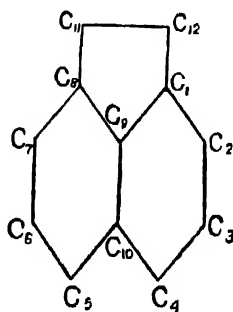
The two aliphatic carbon atoms (11) and (12) are connected by a single bond. In aliphatic compounds, however, we know that the angle between two bonds is the tetrahedral angle of nearly $109°$ and the C-C distance is $1.54 A°$ but as drawn here the angle between $C_8 C_{11}$ and $C_{11} C_{12}$ is apparently a right angle and the distance $C_{11} C_{12}$ appears to be much greater than $1.54 A°$. But if the aliphatic distance is to be preserved between these two carbon atoms the bonds $C_8 C_{11}$ and $C_1 C_{12}$ should be inclined from the symmetrical position. So it is interesting to see whether the atoms lie in the symmetrical positions, or in positions demanded by the aliphatic C-C distance or in positions different from both.

Space-group of Acenaphthene. Acenaphthene crystals belong to the orthorhombic bipyramidal class. The axial lengths as determined by us are

$$a_0 = 8.32 A° \; ; \; b_0 = 14.15 A° \; ; \; and \; c_0 = 7.26 A°$$

and the number of molecules per unit cell is 4. These values are in agreement with those determined by W. H. Bragg. The space-group was found to be $D_{2h}^5 p\gamma\mu\mu$ previously by Hertel and Kleu [6] from a few X-ray reflections. As we have an oscillation camera of high resolving power (diameter 17.18 cm.) it became possible for us to identify an extremely large number of reflecting planes and thereby to determine the space-group unequivocally. A list of the reflecting

planes thus identified are given in Table I. It will be seen from the table that the 'ausloschungen' observed by Hertel and Kleu are completely verified, *viz.*, that planes of the type o k l with l odd are absent. There are no other systematic 'ausloschungen.' This shows that the bc plane is a glide plane of symmetry with glide component along the 'c' axis, the other two axial planes being ordinary planes of symmetry.

As there are four molecules in the unit cell the possible molecular symmetry according to Astbury and Yardley's [7] tabulated results on space-groups, is either a two fold axis normal to o1o or a plane of symmetry parallel to o1o or oo1.

<div align="center">

TABLE I.

List of reflecting planes for acenaphthene
(Oscillation about 'b' and 'c' axes).

Axial planes.

</div>

Plane.	Intensity.	Plane.	Intensity.
0 0 2	v.s.	0 9 0	v.w.
0 0 4	s.	0 10 0	w.
0 0 6	s.	0 11 0	m.
0 3 0	m.s.	2 0 0	s.
0 4 0	v.s.	3 0 0	m.s.
0 7 0	m.w.	4 0 0	m.w.
0 8 0	v.s.	5 0 0	m.s.
		6 0 0	v.v.w.

<div align="center">

Prism Planes.

</div>

Plane.	Intensity.	Plane.	Intensity.
0 1 2	v. s.	0 3 2	m.
0 1 4	v. s.	0 3 4	m.
0 1 6	m.	0 3 6	v. w.
0 2 2	m.	0 4 2	w.
0 2 4	m.	0 4 6	w.
0 2 6	w.	0 5 2	s.

Prism Planes (contd.).

Plane.	Intensity.	Plane	Intensity.
0 5 6	m.	4 0 4	m.
0 6 2	v.s.	4 0 5	m.
0 7 2	s.	4 0 6	m.
0 8 2	m. w.	4 0 7	m.
0 9 2	m. w.	5 0 1	s.
0 10 2	w.	5 0 2	m.
0 11 2	m. w.	5 0 3	m.
0 12 2	m.	5 0 4	m.
1 0 1	s.	5 0 5	m.w.
1 0 2	v. s.	5 0 7	m.w.
1 0 3	s.	6 0 1	w.
1 0 4	s.	6 0 2	m.
1 0 5	s.	6 0 3	m.
1 0 6	m. w.	6 0 4	m.w.
1 0 7	m. w.	6 0 5	m.
2 0 1	v.s.	7 0 1	v.w.
2 0 2	s.	7 0 2	m.
2 0 3	s.	7 0 3	m.
2 0 4	m.	7 0 4	m.
2 0 5	m.	8 0 1	m.w.
2 0 6	m.w.	8 0 2	w.
3 0 1	s.	8 0 3	m.w.
3 0 2	s.	8 0 4	m.w.
3 0 3	m.	9 0 2	w.
3 0 4	w.	9 0 3	w.
3 0 5	v.w	1 2 0	v.s.
3 0 6	w.	1 3 0	s.
4 0 1	s.	1 4 0	m.
4 0 2	s.	1 5 0	m.w.
4 0 3	m.	1 6 0	m.w.

Prism Planes (contd.).

Plane.	Intensity.	Plane.	Intensity.
1 7 0	w.	3 13 0	v. v. w.
1 8 0	m.	4 1 0	m.
1 9 0	w.	4 1 0	m.
1 10 0	m.w.	4 3 0	v. w.
1 11 0	m.w.	4 4 0	v. w.
1 13 0	w.	4 5 0	w.
1 14 0	v. v. w.	4 6 0	m. w.
2 1 0	s.	4 7	m.
2 3 0	m.	4 8 0	w.
2 4 0	m. w.	4 9 0	v. v. w.
2 5 0	m.	4 10 0	v. v. w.
2 6 0	s.	4 12 0	v. w.
7 0	m.w.	4 13 0	v. w.
2 8 0	v. w.	4 14 0	v. w.
2 10 0	v. w.	5 1 0	m.
2 11 0	v. w.	5 2 0	m. w.
2 12 0	w.	5 3 0	w.
2 13 0	w.	5 4 0	m.
3 1 0	m.	5 5 0	m. w.
3 2 0	s.	5 6 0	s.
3 3 0	v. v. w.	5 7 0	w.
3 4 0	m. w.	5 10 0	w.
3 5 0	s.	5 11 0	w
3 6 0	m.	5 13 0	w.
3 7 0	w.	5 14 0	w.
3 8 0	v. w.	6 1 0	m. w.
3 9 0	v. v. w.	6 2 0	m. w.
3 10 3	m. w.	6 3 0	w.
3 11 0	w.	6 4 0	v. v. w.
3 12 0	m. w.	6 5 0	m. w.

Prism Planes (contd.).

Plane.	Intensity.	Plane.	Intensity.
6 6 0	v. v. w.	7 11 0	w.
6 7 0	v. v. w.	8 2 0	m.
6 9 0	v. w.	8 3 0	v. w.
7 1 0	m.	8 6 0	v. w.
7 3 0	m. w.	9 4 0	v. w.
7 5 0	v. v. w.	9 6 0	m
7 6 0	m. w.	10 4 0	w.
7 10 0	w.		

General Planes

Plane.	Intensity.	Plane.	Intensity.
1 1 1	v. s.	1 5 2	s.
1 1 2	s.	1 5 3	v. s.
1 1 3	m.	1 5 4	m.
1 1 4	m. w.	1 5 5	v. w.
1 1 5	w.	1 6 1	m. w.
1 1 6	v. v. w.	1 6 2	m. w.
1 2 1	m.	1 6 3	w.
1 2 2	m.	1 6 4	w.
1 2 3	v. w.	1 6 5	s.
1 2 6	v. v. w.	1 6 6	s.
1 3 1	v. s.	1 6 7	w.
1 3 2	m.	1 6 8	w.
1 3 3	m. w.	1 7 1	s.
1 4 2	m. w.	1 7 2	m. w.
1 4 3	s.	1 7 3	m.
1 4 4	v. v. w.	1 8 1	m. w.
1 5 1	v. s.	1 8 2	m. w.

General Planes (contd.).

Plane.	Intensity.	Plane.	Intensity.
1 8 3	v. v. w.	2 4 2	s.
1 9 1	w.	2 4 3	v. w.
1 9 2	m. w.	2 4 4	m. w.
1 10 1	m. w.	2 4 5	w.
1 10 2	v. w.	2 4 6	v. v. w.
1 10 3	m. w.	2 4 7	v. w.
1 11 1	s.	2 5 1	m.
1 11 2	w.	2 5 2	m. w.
1 11 3	w.	2 5 3	m.
1 12 2	w.	2 5 4	s.
1 12 3	m.	2 5 5	m.
1 13 1	m. w.	2 5 6	m.
2 1 1	v. s.	2 5 7	v. w.
2 1 2	s.	2 5 8	m. w.
2 1 3	m.	2 6 1	v. s.
2 1 4	m. w.	2 6 2	v. s.
2 1 5	m.	2 6 3	v. s.
2 1 8	v. w.	2 6 4	s.
2 2 1	v. s.	2 6 5	w.
2 2 2	m. w.	2 6 7	v. w.
2 2 3	s.	2 7 1	m.
2 2 4	v. w.	2 7 2	w.
2 2 5	w.	2 7 3	m. w.
2 3 1	m.	2 8 1	m.
2 3 2	w.	2 8 2	v. w.
2 3 3	m. w.	2 8 3	m. w.
2 3 4	v. w.	2 9 1	w.
2 3 5	w.	2 10 1	v. w.
2 3 7	v. v. w.	2 10 5	v. w.
2 4 1	m.	2 11 1	v. w.

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General Planes (contd.).

Plane.	Intensity.	Plane.	Intensity.
2 11 2	v. w.	3 4 5	w.
2 11 3	v. w.	3 4 6	v. w.
2 12 1	w.	3 5 1	v. s.
2 12 2	w.	3 5 2	s.
2 12 3	w.	3 5 3	m.
2 13 1	v. w.	3 5 4	m.
2 13 2	v. w.	3 5 5	w.
2 14 2	v. w.	3 6 1	w.
2 14 3	v. w.	3 6 2	
3 1 1	m.	3 6 3	m. w.
3 1 2	s.	3 6 4	m.
3 1 3	s.	3 6 5	m. w.
3 1 4	v. w.	3 6 6	w.
3 1 5	v. w.	3 6 7	v. w.
3 1 6	v. w.	3 7 1	m. w.
3 2 1	m. w.	3 7 2	v. w.
3 2 2	v. w.	3 7 3	m.
3 2 3	v. v. w.	3 8 3	w.
3 2 4	v. w.	3 9 1	m. w.
3 3 1	m.	3 9 2	m. w.
3 3 2	m.	3 10 1	w.
3 3 3	v. w.	3 10 2	w.
3 3 4	w.	3 10 3	w.
3 3 5	w.	3 11 1	w.
3 3 7	v. w.	3 11 2	m. w.
3 3 8	m.	3 11 3	v. w.
3 4 1	m.	3 12 1	m. w.
3 4 2	m. w.	3 12 2	m. w.
3 4 3	m. w.	3 12 3	w.
3 4 4	w.	3 13 1	v. w.

General Planes (contd.).

Planes.	Intensity.	Planes.	Intensity.
3 13 2	v. w.	4 7 3	w.
3 13 3	w.	4 8 1	w.
4 1 1	m.	4 8 2	v. w.
4 1 2	s.	4 9 1	v. v. w.
4 1 3	s.	4 9 2	v. w.
4 1 4	m.	4 9 3	v. w.
4 1 5	w.	4 10 2	m. w.
4 2 1	m. w.	4 11 1	w.
4 2 2	m.	4 11 2	m. w.
4 2 4	w.	4 11 3	w.
4 2 5	v. w.	4 12 2	w.
4 2 6	v. w.	4 12 3	v. w.
4 3 1	m, w.	4 13 1	v. v. w.
4 3 2	w.	4 13 2	w.
4 3 3	v. w.	4 13 3	w.
4 3 4	w.	5 1 1	m.
4 4 1	w.	5 1 2	m. w.
4 4 2	v. w.	5 1 3	m. w
4 4 4	v. w.	5 1 4	v. w.
4 5 1	m.	5 1 5	v. w.
4 5 2	v. w.	5 1 6	v. w.
4 5 3	v. w.	5 2 2	v. v. w.
4 5 4	m. w.	5 2 3	m. w.
4 5 7	v. w.	5 2 4	v. v. w.
4 6 1	m.	5 3 1	m. w.
4 6 2	m. w.	5 3 3	v. w.
4 6 3	w.	5 3 4	w.
4 6 4	m. w.	5 3 5	v. w.
4 6 6	m, w.	5 4 1	v. w.
4 7 1	w.	5 4 5	v. w.

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General Planes (*contd.*).

Planes.	Intensity.	Planes.	Intensity.
5 4 6	v. w.	5 13 1	v. w.
5 5 1	v. w.	6 1 1	m.
5 5 2	s.	6 1 2	m. w.
5 5 3	m. w.	6 1 3	m. w.
5 5 4	m. w.	6 1 4	v. w.
5 5 5	v. v. w.	6 1 5	v. w.
5 5 6	v. w.	6 2 1	w.
5 5 7	w.	6 2 2	v. w.
5 6 1	m.	6 2 3	m.
5 6 2	s.	6 2 5	v. v. w.
5 6 3	m.	6 3 1	m. w.
5 6 4	w.	6 3 2	m. w.
5 6 5	w.	6 3 3	v. v. w.
5 6 6	w.	6 3 4	v. w.
5 7 1	m. w.	6 3 5	v. v. w.
5 7 2	m. w.	6 4 1	v. w.
5 7 3	w.	6 4 2	v. w.
5 8 1	m. w.	6 4 3	m. w.
5 8 2	w.	6 5 1	s.
5 8 3	m. w.	6 5 2	m. w.
5 9 1	m. w.	6 5 3	m. w.
5 9 2	w.	6 5 4	m. w.
5 10 1	v. w.	6 5 5	m.
5 10 2	m. w.	6 6 1	m.
5 10 3	m. w.	6 6 2	m. w.
5 11 1	w.	6 6 3	m.
5 11 3	w.	6 6 4	w.
5 12 1	w.	6 6 5	m. w.
5 12 2	w.	6 6 6	m. w.
5 12 3	w.	6 7 1	m. w.

General Planes (contd.)

Planes.	Intensity.	Planes.	Intensity.
6 7 2	w.	7 5 4	w.
6½ 7 3	w.	7 6 1	m. w.
6 8 1	v. v. w.	7 6 2	w.
6 8 3	w.	7 6 3	m. w.
6 9 2	v. v. w.	7 6 4	w.
6 9 3	v. v. w.	7 7 1	v. w.
6 11 1	v. v. w.	7 7 2	w.
6 11 2	w.	7 8 2	w.
6 11 3	w.	7 9 2	w.
6 12 1	w.	7 10 3	w.
6 12 2	w.	7 11 1	v. v. w.
7 1 2	v. w.	8 1 1	w.
7 1 3	w.	8 1 2	w.
7 1 4	v. w.	8 1 4	m. w.
7 1 6	v. w.	8 2 2	v. v. w.
7 2 1	v. w.	8 3 1	v. w.
7 2 2	v. w.	8 4 1	v. v. w.
7 2 3	w.	8 4 2	v. w.
7 2 4	v. w.	8 5 1	v. v. w.
7 3 1	w.	8 5 2	m. w.
7 3 2	v. w.	8 5 3	w.
7 3 3	v. v. w.	8 6 1	v. w.
7 3 4	v. w.	8 6 2	m. w.
7 4 1	v. w.	8 6 3	v. w.
7 4 2	v. w.	8 7 1	v. w.
7 4 3	v. v. w.	8 7 2	s.
7 4 4	v. v. w.	8 8 2	s.
7 5 1	v. w.	9 1 2	v. w.
7 5 2	m. w.	9 4 1	v. w.
7 5 3	m. w.	9 4 2	w.

General Planes (contd.).

Plane.	Intensity.	Plane.	Intensity.
9 5 1	v. w.	10 1 2	v. w.
9 5 2	m. w.	10 2 2	v. w.
9 6 1	m. w.	10 4 1	v. w.
9 6 2	w.		

Atomic Arrangement in Acenaphthene.

As we have seen before from its space-group, acenaphthene molecule must possess either a plane of symmetry parallel to the ' b ' or the ' c ' face or an axis of symmetry normal to the ' b '-face. Thus we have to try three classes of arrangements and let us call them respectively as class ' A,' class ' B ' and class ' C.' From the stereochemical formula of acenaphthene it is seen that the two-fold axis if there be one should pass through C_9C_{10}. On the other hand if the molecule possesses a plane of symmetry, the plane of symmetry must be either the plane containing the naphthalene nucleus or the plane normal to that through C_9C_{10}.

Class A.—*The molecule possessing a plane of symmetry parallel to the ' b '-face.* Two cases may arise according to whether the plane of the naphthalene nucleus or its normal is the plane of symmetry. In the first alternative, the plane of the molecule is the ' b '-face. In that case the diamagnetic susceptibility along the ' b ' axis should be the maximum, but on the contrary it is the minimum as found by Krishnan, Guha and Banerjee.[5] So we may discard this type of orientation as untenable. According to the other case in this class the length of the molecule should be parallel to the ' b ' axis as it is normal to the plane of symmetry. The gram molecular diamagnetic susceptibility in this direction should be equal to that of naphthalene along the length of the molecule but for the modification due to the two CH_2 groups at the side. It is highly improbable that only the two CH_2 groups at the side can modify the gram molecular susceptibility in this direction from -39.4 to -72.1. There is another difficulty which makes this orientation impossible. In acenaphthene crystal all the three axial planes are planes of symmetry. In the orientation that we are considering, since the ' b ' plane is a molecular plane of symmetry the other two planes of symmetry are brought about by repetitions of molecules. So we have to accommodate cross-sections of four molecules within the ' b '-face of the unit cell which is too small for that. Thus the possibility of a plane of symmetry parallel to the ' b '-face is precluded.

Class 'B'.—*The molecule possessing a plane of symmetry parallel to the 'c'-face.* Here also as before two cases arise. The first case is that the molecular plane is parallel to the 'c'-face. The gram molecular susceptibility in this case should be maximum along 'c' and its value should not be less than that for the direction normal to the naphthalene molecule since the average value (111·8) for the molecule is much greater than that for naphthalene (89·8). But though it has been found to be the maximum along the 'c' axis its value is $-145·6 \times 10^{-6}$ while that for normal to the naphthalene molecule is $-187·2 \times 10^{-6}$. The other case is precluded by the fact that in this case the length of the molecule should be along the 'c' axis and consequently the molecular susceptibility should be the minimum while actually it is the maximum.

Class 'C'.—Thus we are left with the only possibility that the 'b' axis is a two fold axis of symmetry of the molecules so that it coincides with $C_9 C_{10}$. In this direction it is probable that the susceptibility of the molecule is altered to some extent from the value for the naphthalene nucleus due to the presence of the two CH_2 groups. As regards the susceptibilities in the other directions agreements may be obtained by rotating the molecule to the requisite amount about the two fold axis.

The mean gram molecular susceptibility of acenaphthene is $-111·8 \times 10^{-6}$ Let the gram molecular susceptibilities along the length, breadth and thickness of the molecule be respectively K_1, K_2 and K_3 then

$$K_1 + K_2 + K_3 = -335·4 \times 10^{-6}.$$

K_2 is the value along the 'b' axis, so that it is $-72·1 \times 10^{-6}$. Hence $K_1 + K_3 = -263·3 \times 10^{-6}$. The value of the corresponding quantity for naphthalene is $-226·6 \times 10^{-6}$.

So if we consider that the CH_2 groups influence K_1 and K_3 equally, we have

$$K_1 = -57·7 \times 10^{-6} \quad \text{and}$$

$$K_3 = -205·5 \times 10^{-6}.$$

Suppose the molecular plane makes an angle α with the 'c'-face then we may write out the following equation correlating the susceptibilities.

$$117·6 = 57·7 \cos^2\alpha + 205·6 \sin^2\alpha$$

whence

$$\alpha = 39° \, 30'$$

5

We have taken from the known structures of the other aromatic compounds the distance between consecutive carbon atoms in the benzene rings to be 1.42 A°, while those between $C_1 - C_{12}$ and $C_{11} - C_{12}$ have been determined by trial. At first the intensities of the axial planes were calculated for the molecular plane at $39\frac{1}{2}°$ with the ' c '-face. By altering the $C_1 C_{12}$ and $C_{11} C_{12}$ distances and the position of the molecule along the ' y '-axis within reasonable limits, it was not possible to get agreement with the estimated intensities. The angle a and these lengths as well as the position of the molecule along the ' b '-axis were then varied until the best agreement could be obtained. For this the angle a is $26°$ and the distance $C_1 C_{12}$ and $C_{11} C_{12}$ are respectively 1.47 A" and 2.01 A°. The atomic parameters for half of a molecule are given in Table II.

TABLE II.

Atomic Parameters in Acenaphthene Crystal.

Atoms.	x.	y.	z.
C_1	0.131	$.280$	$.072$
C_2	$.261$	$.239$	$.144$
C_3	$.261$	$.139$	$.144$
C_4	$.131$	$.089$	$.072$
C_9	0	$.239$	0
C_{10}	0	$.139$	0
C_{12}	$.111$	$.400$	$.061$

The nature of agreement for the axial planes can be seen from the Table III, in which the first column gives the planes, the second column gives calculated structure factors and the third column gives the estimated intensities. For the calculations, the atomic structure factors for the aromatic carbon atoms were taken from the table given by Robertson (*Proc. Roy. Soc.*, Vol. 150A, p. 110, 1935) and for the aliphatic carbon atoms, the values given by Ponte for diamond were adopted (*Phil. Mag.*, Vol. 3, p. 195, 1927).

From the above discussions we find that the distance $C_8 C_{11} = C_1 C_{12} = 1.47$A°, and $C_{11} C_{12} = 2.01$A°. The angle $C_8 C_{11} C_{12} =$ the angle $C_1 C_{12} C_{11} = 97°$ and the angle $C_9 C_8 C_{11} =$ the angle $C_9 C_1 C_{12} = 114°$. Thus we see that the bonds $C_8 C_{11}$

<div align="center">

TABLE III.

Calculated and observed Intensities of Reflection.

</div>

Indices.	Calculated Structure Factor.	Estimated Intensities.
200	$- 26.2$	s
300	$- 11.7$	ms
400	$- 7.2$	mw
500	$- 32.3$	ms
600	$- 3.4$	vvw
030	$- 19.4$	ms
040	$- 32.2$	vs
050	$- 11.6$	Not observed.
060	5.9	
070	$- 11.1$	mw
080	41.8	vs
090	$- 15.5$	vw
0(10)0	8.3	w
0(11)0	$- 19.0$	m
002	72.3	vs
004	17.2	s
006	$- 16.1$	s

and C_1C_{12} have properties intermediate between aliphatic and aromatic carbon atoms, both as regards angle and size, while the purely aliphatic bond $C_{11}C_{12}$ has been lengthened out.

<div align="center">

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DIELECTRIC CONSTANT OF AN ELECTRONIC ATMOSPHERE FOR ULTRA-SHORT WAVES

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ABSTRACT. Measurements of the dielectric constant of an electronic medium between he plate and the filament of a dull-emitting screen-grid valve (and also of a triode) have been made for different thermionic currents and for a certain range of ultra-short wave-lengths. The dielectric constant has been found first to decrease and then to increase with the increasing values of the thermionic current. This variation has been explained in view of certain characteristic features associated with the thermionic valves.

The dielectric constant of the electronic medium has been found to decrease with the wave-length for the shorter wave-lengths. This variation is not in perfect agreement with the Eccles-Larmor formula Beyond a certain wave-length the dielectric constant of the medium increases again with the wave-length. The unmistakable turning point in the dielectric constant-wave-length curve suggests some kind of resonance effect.

1. INTRODUCTION.

Experimenting with pure electronic atmosphere obtained by heating a metal filament in a vacuum, Benham [1] and Bergmann and Düring [2] showed that the dielectric constant would be less than unity. Repeating Bergmann and Düring's experiments Sil [3] observed that the value of the dielectric constant would be sometimes less, sometimes greater than and sometimes equal to unity. Most of these investigations are of a qualitative nature. Recently Prasad and Verma [4] have published some experimental results with an electron atmosphere in a screen-grid valve, employing longer wave-lengths (81 m. to 520 m.). Their results show a quantitative agreement with the Eccles-Larmor theory.

The object of the present investigation has been to measure the dielectric constant of an electronic medium between the plate and the filament of a thermionic valve for different electronic concentrations and for a certain range of ultra-short weve-lengths. In interpreting these experimental results, due consideration has been given to the non-uniform distribution of electrons in the space between the plate and the filament of the thermionic valve and also to the finite time which elapses between the entry of the electrons into the inter-electrode space and their absorption by the plate.

2. METHOD AND SCOPE OF THE INVESTIGATION.

Briefly the method has been to set up an ultra-short wave oscillatory circuit with a suitable coil and a capacity. The capacity is the plate-filament capacity of a thermionic valve. A Lecher wire system inductively coupled to the coil of the oscillating circuit measures accurately the change in the wave-length of the oscillation due to the change in the inter-electrode capacity when a thermionic current is passed between the plate and the filament. The dielectric constant of the electronic medium in the thermionic valve can be calculated from the measurement of the wave-lengths when the thermionic current is off and on. If L be the inductance of the coil and C the capacity of the condenser in the oscillatory circuit, the wave-length is given

$$\lambda = A \sqrt{L.C} \; *$$

where A is a constant. The value of C is changed to C′ when the space between the plate and the filament is filled with an electronic atmosphere. The wave-length of the oscillation is therefore modified. The modified wave-length is then given by

$$\lambda' = A \sqrt{L.C'}$$

so that the dielectric constant of the medium is given by

$$K = \frac{C'}{C} = \frac{\lambda'^2}{\lambda^2}$$

According to Eccles-Larmor theory

$$K = 1 - \frac{4\pi N e^2}{m(\omega^2 + \nu^2)}$$

* We have neglected here the interaction of the oscillating valve on the oscillatory circuit.

where

      ω=angular frequency of the oscillation,

      ν=collision frequency of the electrons,

      N =electron density.

      e and m are the charge and mass of an electron.

Since the collision frequency ν can be neglected in a high vacuum valve

$$\frac{\lambda^2 - \lambda'^2}{\lambda^2} = \frac{4\pi N e^2}{r^2} \cdot \lambda^2$$

or

$$\frac{\lambda^2 - \lambda'^2}{\lambda^4} = \frac{4\pi N e^2}{mc^2}$$

The electron-density N can be calculated from this relation.

Two distinct sets of experiments have been performed.

(1) Keeping the wave-length of the valve-oscillator constant, the thermionic current has been varied and the shift of the tuning point of the Lecher wire system accurately measured. Thus for different thermionic currents, the values of the dielectric constant have been estimated from these measured shifts.

(2) Keeping the thermionic current constant, the wave-length of the valve oscillator has been varied over a certain range and wave-length-measurements made with the thermionic current on and off.

The plate-filament capacity of a dull-emitting screen-grid valve (P. M. 14) has been employed in this investigation. Similar inter-electrode capacity of a bright-emitting triode valve (' Ora ' valve) has also been tried.

3. EXPERIMENTAL ARRANGEMENTS.

The circuit arrangement adopted in the measurement of the dielectric constant of an electronic medium inside a thermionic valve is shown in figures 1(a) and 1(b). The oscillatory circuit consists of a single turn 2″ to 3″ in diameter of 1/8″ copper tube L and the plate-filament capacity A F of a screen-grid tetrode or a triode valve. A small variable condenser C_1 has been employed for retroaction while suitable choke coils having self-resonance at approximately the working wave-length have been used in all the direct current supply leads to the valve electrodes. A Philips T. C. 03/5 valve with a suitable grid-bias has been employed for generating the ultra-short waves. The single turn of the copper tube has been coupled loosely to another loop the two ends of which are connected to the ends of a pair of parallel Lecher wires (No. 18 bare copper wire). The wave-

(a)

(b)
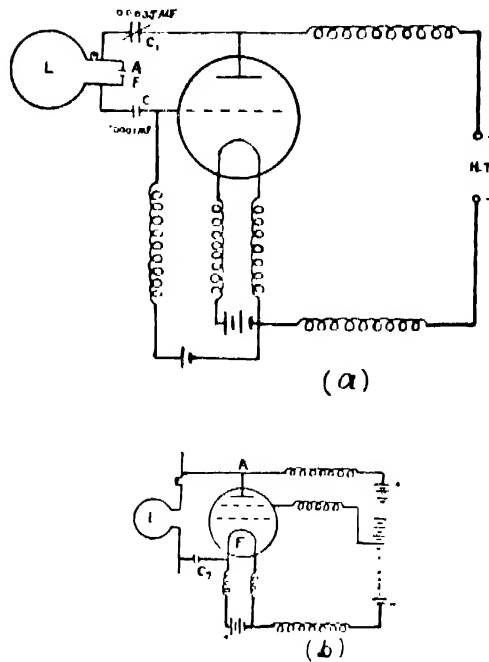
FIGURE 1.

length of the oscillation can be accurately measured by the Lecher wire system. For accuracy of measurements a third parallel wire fitted with a long wooden scale running parallel to it has been fixed closed to one of the two Lecher wires. A copper bridge mounted on a suitable ebonite handle can be moved across the pair of Lecher wires and the position of the bridge noted for resonance by observing the quenching of a small lamp in the oscillatory circuit. A telescope has been used for the observations whenever necessary. An A. C. milli-ammeter has also been used for determining the positions of resonance. The ammeter has been suspended from the Lecher wires by two vertical rods of the same size, the upper ends of which slide along the wires and the lower ends of which are rigidly fixed to the terminals of the ammeter. The ammeter has been allowed to rest on a suitable stand. A slider with a pointer is then fixed on the third measuring wire and the scale reading noted for the position of resonance. The next position for resonance can be determined in a similar way and fixed by another slider on the measuring wire. The wave-length is determined by doubling the distance between the two consecutive positions.

Since it is necessary to apply a high voltage to the anode of the valve, the inter-electrode capacity of which is under examination, a neutrodyne condenser C_2 has been placed in the loop circuit in order to avoid short circuit through it. Another condenser C has been inserted to protect the grid of the oscillating valve. With suitable high voltages to the anode and the screen grid of the valve

the wave-lengths of the oscillations have been accurately determined with the filament current off and on. The dielectric constant of the medium is then calculated from the observed change in the wave-length of the oscillation.

4. MEASUREMENTS OF THE DIELECTRIC CONSTANT OF THE ELECTRONIC ATMOSPHERE FOR DIFFERENT THERMIONIC CURRENTS.

Measurements of the dielectric constant of the electronic medium between the filament and plate of the two thermionic valves have been made for different values of the plate curent. In the case of the bright emitting triode valve (the "Ora" valve) the plate current has been varied by varying the plate voltage and in the case of the screen-grid valve, the plate current has been changed by changing the screen-grid voltage. The variation of the plate current by varying the filament current has also been tried in the latter case.

'Ora' value
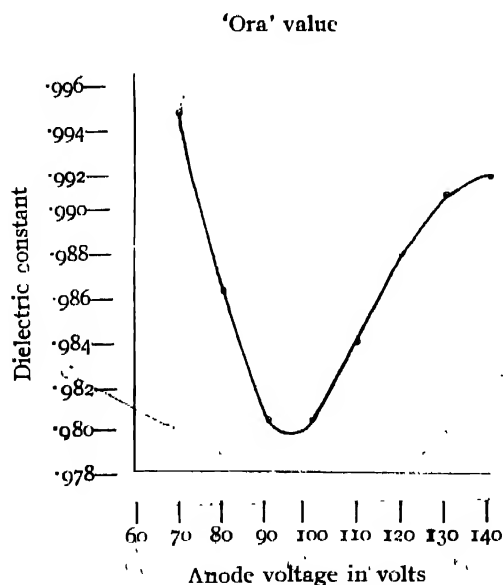
FIGURE 2.

These experimental results are illustrated in figures 2, 3, 4 and 5, all of which show that the dielectric constant of the electronic medium decreases at first and subsequently increases with the increasing values of the thermionic current. The values of the electron density are on calculation found to be of the order of 10⁸ per c. c.

6

Mullard P.M. 14 vavle
λ = 425 cm.

FIGURE 3.

Mullard P.M. 14
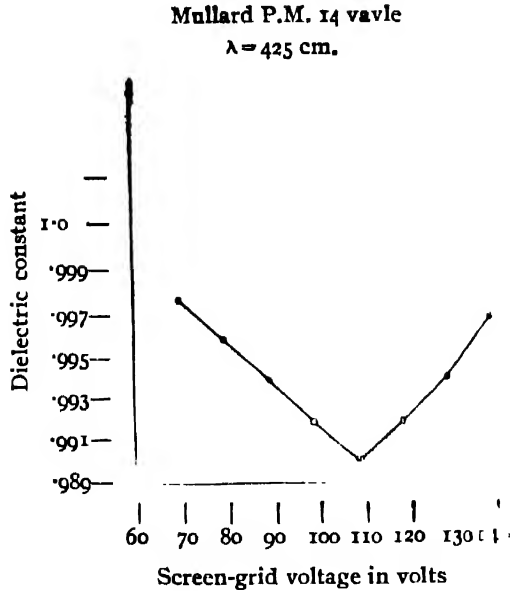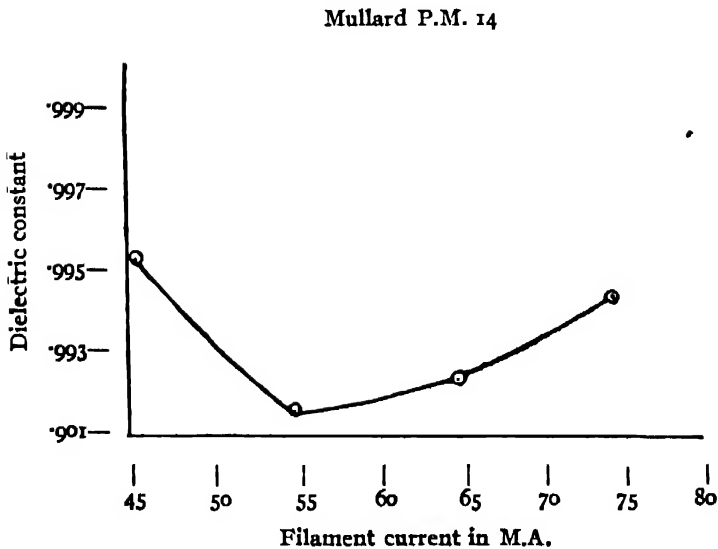
FIGURE 4.

It is to be noted here that in the case of the bright-emitting " Ora " triode valve it has been tested whether the change in the inter-electrode capacity is due to the heating effect of the filament. The current has been found to raise the temperature of the outside glass surface of the valve to about 40°C, *i.e.*, about 10° above the room temperature in about 15 sec. By placing a high power electric lamp

Mullard P.M, 14 valve
λ=469·4 cm.
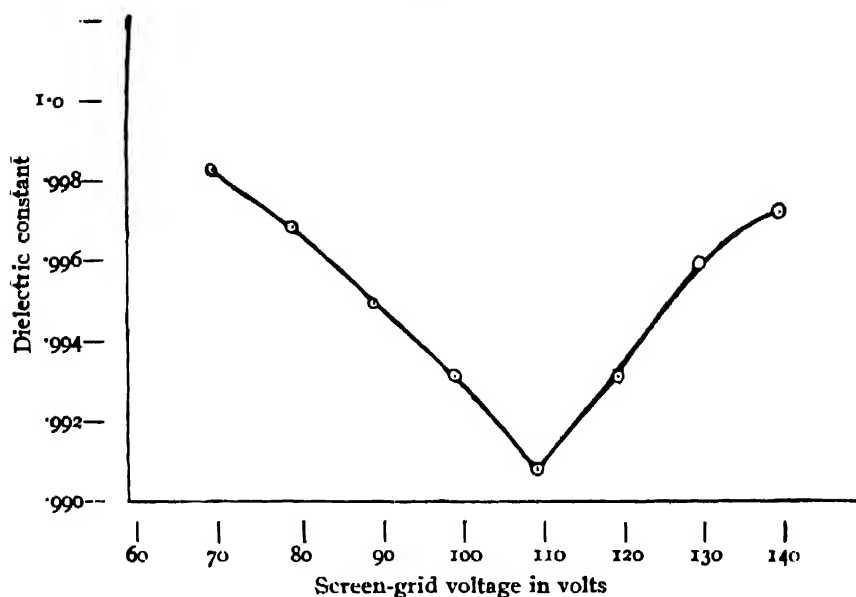
FIGURE 5(a).

Mullard P.M. 14, λ=516·8 cm.
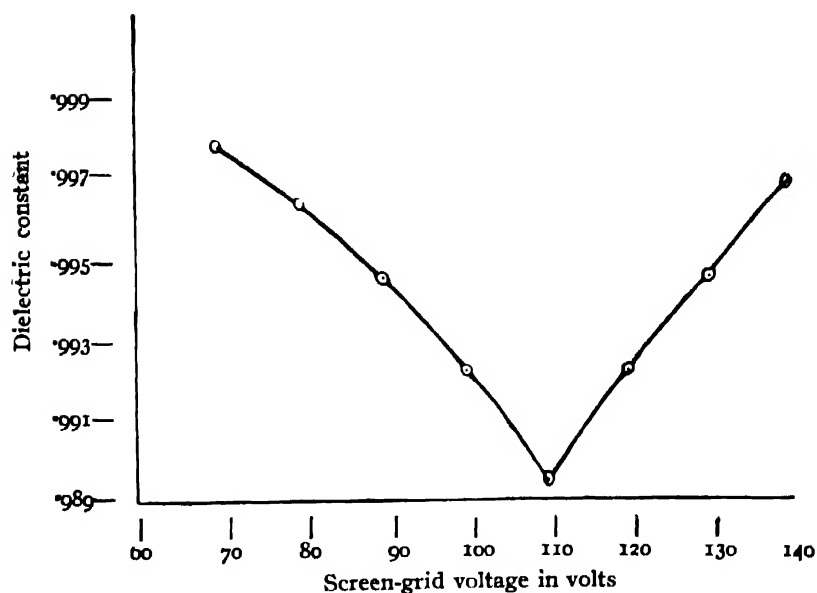
FIGURE 5(b).

near the valve, the temperature of the outside of the valve could be raised to above 90°C. It has been shown that raising the temperature to 40°C does not

affect the wave-length of the oscillation. While doing this test, the oscillatory circuit has been protected from the heat of the electric lamp. Further, it has been found that when the grid-plate capacity has been inserted in the oscillatory circuit and the plate disconnected from the high voltage the wave-length of the oscillation remains the same, whether the filament is off or on. (The filament is about ·3cm. away from the grid.) This negative result is a test that the temperature effect on the inter-electrode capacity is negligible. As soon as the plate is connected to the high voltage and the filament is on, the wave-length has been found to be definitely shorter showing that the value of the dielectric constant is less than one.

5. INTERPRETATION OF THE ABOVE RESULTS.

There are factors which should be taken into consideration in interpreting the experimental results with the thermionic valves. Firstly the distribution of electrons is not uniform in the space between the filament and the plate in a valve under the conditions of the experiments and an increase of the plate current does not necessarily mean an increase in the average electron-density in the inter-electrode space. Secondly, the time which elapses between the entry of the electrons into the inter-electrode space and their absorption by the plate is finite, while we know that for the Eccles-Larmor formula to hold, the electrons should remain in the space between the electrodes for an indefinite period or at least for an interval of time long compared with the period of oscillations. We shall consider the latter effect first.

(1) *The effect of the time of stay of the electrons in the inter-electrode space on the dielectric constant of the electronic medium:*

If T be the time of stay of the electrons, Benner [7] has shown that the change in the dielectric constant will be given by

$$\Delta K = -\frac{4\pi N e^2}{m\omega^2}\left(1 - \frac{\sin \omega T}{\omega T}\right)$$

As the plate voltage in our experiments with the triode or as the screen grid voltage in the experiments with the screen-grid tetrode has been increased gradually, it is evident that the time of stay T of the electrons in the inter-electrode space will be gradually diminished. On inspecting Benner's formula, it will be found that the change of dielectric constant will also gradually decrease with the increase of the plate voltage or the screen-grid voltage. We shall give here an approximate estimate of the time of transit of the electrons.

Let the plate voltage V of a triode valve be 50 volts. Then since $e.V = \frac{1}{2}mv^2$, where e, m and v are the charge mass and velocity of the electron.

$$v = 4·2 \times 10^8 \text{cm/sec.}$$

The time of transit* will then be given by

$$T = \frac{\text{Distance between the filament and plate}}{\text{velocity of the electrons}}$$

$$= \frac{.3}{4.2 \times 10^8} = .71 \times 10^{-9} \text{ sec.}$$

Similar calculations for the plate voltage $= 150$ V show

$$T = .39 \times 10^{-9} \text{ sec.}$$

In table I are given the calculated values of $\left(1 - \dfrac{\sin \omega T}{\omega T}\right)$ for various values of T and ωT. We have taken $\omega = 4.71 \times 10^8$ ($\lambda = 4$m). This is illustrated in figure 6.
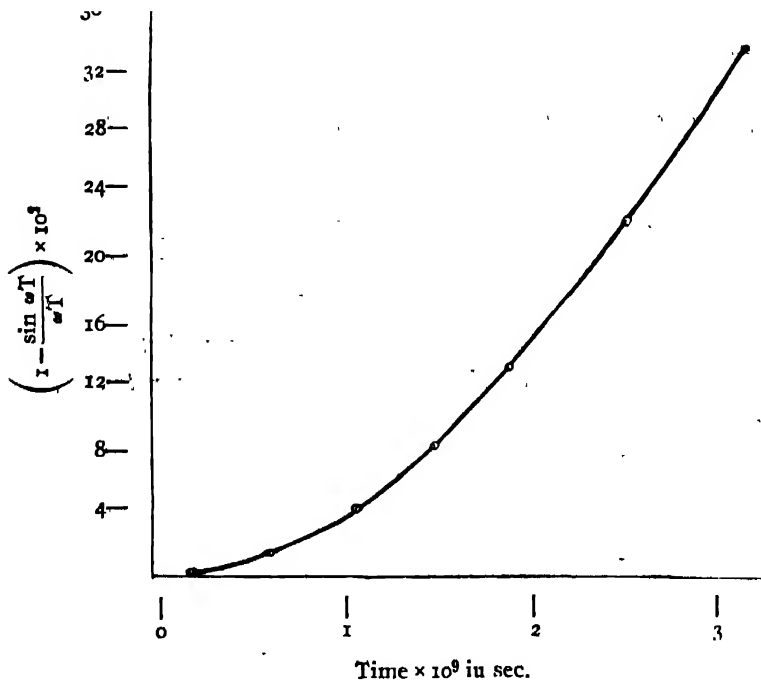
FIGURE 6.

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* A more detailed calculation of the time of transit taking into consideration the cylindrical shape of the plate can however be made according to Mitra and Sil's formula (Phil. Mag. 7, XIII, p. 1081, 1932).

TABLE I.

T.	ωT.	$\left(1 - \frac{\sin \omega T}{\omega T}\right).$
$\cdot 22 \times 10^{-9}$ sec.	$\cdot 105$	$\cdot 002$
$\cdot 63$,, ,,	$\cdot 297$	$\cdot 015$
$1 \cdot 07$,, ,,	$\cdot 506$	$\cdot 043$
$1 \cdot 52$,, ,,	$\cdot 716$	$\cdot 083$
$1 \cdot 91$,, ,,	$\cdot 908$	$\cdot 132$
$2 \cdot 66$,, ,,	$1 \cdot 204$	$\cdot 225$
$3 \cdot 19$,, ,,	$1 \cdot 501$	$\cdot 336$

The greater the plate voltage (or the screen-grid voltage), the smaller is T and hence less is the decrease in the value of the dielectric constant. In other words the dielectric constant will increase with the voltage.

(2) *The effect of non-uniform distribution of electrons in the inter-electrode space :*

With smaller plate voltage (or the screen-grid voltage) the electron density near the filament is much greater than elsewhere. With the increase of the plate-voltage (or the screen-grid voltage) there is less of this non-uniformity. Following Sil's arguments[6] it can be said that a *non-uniform distribution of the conductivity increases the value of the effective dielectric constant of the electronic medium.*

It is therefore expected that the dielectric constant will gradually decrease and may even attain a minimum value, as there is more of uniformity in the electron distribution when the plate voltage (or the screen-grid voltage) is gradually increased.

Thus taking into consideration the effect of non-uniformity of the electron distribution which is predominent at lower voltages as well as the effect of the time of transit of the electrons on the value of the dielectric constant, we may expect initially a decrease of the dielectric constant and subsequently an increase as the plate-voltage or the screen-grid voltage is gradually increased. This is what has been observed in our experiments. (see figures 2, 3 and 4).

In the experiments where the dielectric constant has been measured for various values of the filament current in a tetrode (keeping the plate-voltage and the screen-grid voltage constant) it can be seen from figure 5 that the dielectric

constant decreases and subsequently increases with the increase of the filament current.

With the increase of the filament current, the electron density in the valve increases. so that the dielectric constant would decrease as the filament current is increased, but here we have also to consider the effect of non-uniform distribution of electrons in the thermionic valve which works in the opposite direction. Since there is more non-uniformity of electron distribution with larger filament current the dielectric constant is expected to increase with larger filament current.

The increase due to the non-uniform distribution may more than counter-balance the decrease of dielectric constant due to larger electron density for the larger values of the filament current. The nature of the experimental curve showing the variation of the dielectric constant with the filament current can therefore be explained.

6. VARIATION OF THE DIELECTRIC CONSTANT OF THE ELECTRONIC MEDIUM WITH THE WAV-ELENGTH OF THE OSCILLATION.

The dielectric constant of the electronic medium between the plate and the filament of a screen-grid valve has been measured for a certain range of wave-lengths. The range of wave-lengths employed lies between 4 m. to 5·1 m. The dielectric constant has been found to decrease below unity and then to gradually increase approaching unity. The observed change of the dielectric constant in he first part of the curve is not strictly proportional to the square of the wave-
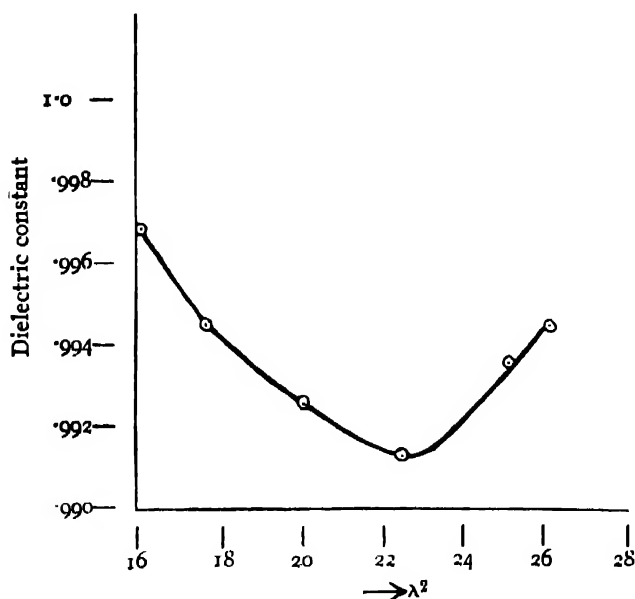
FIGURE 7.

length. The agreement with the Eccles-Larmor formula is not therefore perfect. The experimental results are illustrated in figure 7.

It is to be mentioned here that Mitra and Banerjee's [7] experiments with a discharge tube and also our own experiments [8] with ionized gases have yielded similar experimental results. According to Mitra and Banerjee the latter part of the curve (showing the anomalous increase of the dielectric constant with the wave-length) is due to the conductivity acquired by the medium. This finite conductivity may be possible in a high vacuum valve as a result of the collision of the electrons against the anode. Usually however in a high vacuum, the collision frequency is neglected and the conductivity term regarded as practically zero.

The curves on the other hand strongly suggest some kind of resonance effect. No definite conclusion can however be reached as to the interpretation of these curves at the present stage of our investigations.

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ON N. R. SEN'S [1] DERIVATION OF THE LORENTZ TRANSFORMATION

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ABSTRACT. It is indicated after a close analysis that the Principle of Equivalence and supplementary hypotheses assumed by N. R. Sen only *apparently* get over the necessity of recognising the constancy of the velocity of light as a separate postulate.

It is well known that all recent fundamental investigations into kinematics and space and time derive their inspiration from the celebrated and subtle memoir of A. Einstein on "The Electrodynamics of Moving Bodies" (1905)[2] in which the author has attempted to replace the *abstract* space and time relationships of classical physics by concrete, *i.e.*, in principle capable of experimental treatment, conceptions. In particular it is pointed out that for two observers A and B there exist an A-time and a B-time in their respective immediate neighbourhood and there is *no* relation between A-time and B-time of an *a priori* nature. The relation between them in this respect is established by *DEFINITION* that the "time" light takes to travel from A to B is equal to the "time" it takes to travel from B to A.

As a consequence of the above definition of "time" the velocity of light between A and B becomes the same *with respect to* the two observers.

Further it is assumed that $\dfrac{2\,AB}{t'_A - t_A} = C$ [3] is a constant in vacuo

the velocity of light is independent of the emitting source and is the same *at every point of free space*.

It is obvious that if the last assumption is not taken into account an element of *indefiniteness* creeps into our *defined* "time" and will introduce a corresponding indefiniteness in the transformations to be obtained.

(See the Appendix.)

With this definition of "time" two operations (a) and (b) are defined on pp. 40-41 of Einstein's paper[4] which co-ordinate results in *the inertial system K with results in the inertial system K'*.

We are now in a position to discuss N. R. Sen's treatment of the subject,

In accordance with his Principle of Equivalence [5] N. R. Sen says :—" We assume two similar clocks at rest at O and O' in the system K and K' respectively. The measurements of unit time interval of each clock in its own system by an observer at rest in the *other* system *MUST* be identical."

From the formal and mathematical standpoints the above statement, of course, assumes no more than a mutual reciprocity of relationships but its application to *physical reality* concedes the following considerations :—

The clock at O (in K) registers an event and simultaneously a light signal is sent to O' (in K') and similarly a second event is registered at O after a unit time interval and the light signal as before, is sent to O'. Likewise the procedure in O' is recorded at O.

Now when we assert that results reached in K and K' *must* be identical it goes with it that we have (amongst other things, like the co-ordination of time intervals) *taken for granted from experience** the constancy of the *average* velocity of light for, at least, the systems *under consideration*, for otherwise it may not be so.

Again a little reflection will show that if the velocity of light be not, as well, assumed to be constant *at every point* of free space an element of *indefiniteness* will enter into the transformations to be deduced (See the Appendix). The principle of continuity invoked by N. R. Sen is, essential'y, an abstract mask for the idea of the constancy of the velocity of light at every point in vacuo.

Thus we find that Sen's treatment *when applied to reality* has to recognise the principle of the constancy of the velocity of light as an additional postulate.

It is possible to start from general logical premises and reach an "abstract" Lorentz transformation but application to the physical world necessitates an explicit (or implicit) recognition of the two postulates of Special Relativity.

In conclusion I wish to thank my friend Mr. Oomar Farooq for valuable hints.

APPENDIX

The idea of indefiniteness in the transformations referred to in the previous discussions needs, perhaps, to be eiucidated for the average reader.

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* That this has to be a *separate* assumption is due to the important fact stressed by Einstein (See the footnote to introduction in his paper "The Foundations of the General Theory of Re ativity," 1916) [¶] that a result may be epistemologically sound but may be in conflict with experience. Without it the formal conclusions are restricted to a philosophical vacuum.

If in Special Relativity it be not assumed (in consonance with experience) that the velocity of light is constant at every point of free space we can have

$$\frac{2AB}{t'_{1\lambda} - t_{\lambda}} = C_1, \ (C_1 + C), \text{ etc.}$$

which results are compatible with the *definition* of time but whose introduction will obvious¹y prevent a *unique* determination of the transformation.

Similarly $C + C_1 \pm C_2$ can satis𝑓y N. R. Sen's Equivalence Principle (since $t'_2 - t'_1 = t_2 - t_1$ and $t'_3 - t'_1 = t_3 - t_1$ are compatible when $t_3 - t_1 + t_2 - t_1$ the signals being, as understood, sent after unit time intervals of each clock) but which naturally lead to an indefiniteness in the transformation formulæ.

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[3] *Ibid.*

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[5] P. 344 of (1).

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A REPLY TO HUSAIN'S NOTE.

By N. R. SEN.

Through the courtesy of the Editors I had an opportunity of looking into Mr. Husain's note. There appears to be some misapprehension which I hope the following paragraphs will dispel.

Mr. Husain concludes by saying "It is possible to start from general logical premises and reach an abstract Lorentz transformation but application to the physical world necessitates an explicit (or implicit) recognition of the two postulates of Special Relativity." There is nothing in my paper to suggest the contrary. But there are two points raised in Mr. Husain's note which require to be elucidated further.

Firstly, synchronisation of *distant* clocks (even in the same system) is carried out *physically* with the assumption of the constancy of the velocity of light, so that our time is physically *defined* by this principle. Thus when we talk of ' time ' in physical (and astronomical) relations we cannot ignore that principle. But the justification for this method of measurement is it does not lead to a contradiction and is most convenient from the point of view of our knowledge of the physical world. My treatment is frankly a logical analysis and an attempt at a logical construction as has several times been stressed by the use of the term *formal* Lorentz transformation and the necessity of contact with reality by experiment. In other words the existence of similar synchronised clocks as well as of suitable methods of measurement are assumed. That the empirical fact of the constancy of the velocity of light is utilised in our actual measurement of time or the electromagnetic wave is used as a causal chain between different systems is not relevant to this particular discussion. In the usual derivation of the transformation there are explicit equations expressing the constancy of the velocity of light *in all systems*. In my note the actual content of the Principle of Equivalence has been investigated by dropping these equations, which makes this content logically independent of any particular mode of measurement. Supplementary hypotheses were made to bring into evidence the existence of a unique velocity characteristic of the Lorentz transformations.

Secondly, it has been suggested in Mr. Husain's note that the " Principle of Continuity," assumed by me " is an abstract mask for the idea of the constancy of the velocity of light at every point in vacuo." By " constancy at every point " (?) is probably implied uniformity. But this suggestion is unwarranted and is hardly true. Continuity is a far more general assumption than

uniformity, and the chances of these two assumptions being identical in source are very remote. The appearance of an undefined velocity V in the transformation is, however, not without expectation. As a form the transformation as yet is void of reality. It is to be made physically realisable by comparison with experience, and it is here that contact with reality is possible.

In the non-homogeneous space, referred to in Mr. Husain's Appendix, the matter will be far less simple, when the question will be of the invariance of $dx^2 - c^2(x)dt^2$. In fact we then have to leave the domain of special Relativity and pass on to General Relativity.

RAMAN EFFECT AT LOW TEMPERATURE : PHOSPHORUS TRICHLORIDE, CYCLOHEXANE AND CHLOROBENZENE.*

By S. C. SIRKAR,

AND

J. GUPTA.

ABSTRACT. The Raman spectra of phosphorus trichloride, cyclohexane and chloro-benzene have been studied in the solid state at the temperature of liquid oxygen. No new lines have been observed in the neighbourhood of the Rayleigh line in the case of the first two subs-tances but in the case of chlorobenzene four new Raman lines having $\Delta \nu$ in cm^{-1} respectively equal to 49, 67, 86 and 105 have been observed at the low temperature The significance of this fact as well is the probable origin of these lines have been discussed in detail In the case of the phosphorus trichloride molecule, all the lines due to the vibrations ν_1, ν_2 ν_3 and ν_4 are slightly shifted at the low temperature from their respective positions at the room tempera-ture and ν_3 gives a sharp line accompanied by two weak satellites at the low temperature. These facts have been discussed from theoretical point of view. In the case of cyclo-hexane, the line 1266 cm^{-1} is split up into two equally intense components at the low temperature showing the twofold degeneracy of the line and confirming the conclusions of Kohlrausch and Stockmair that the probable symmetry of the molecule is S_{6u}.

INTRODUCTION.

It was first observed by Gross and Vuks[1] that when certain organic subs-tances which are liquids at the room temperature are solidified, some new Raman lines having small frequency shifts appear in the scattered spectrum of each of these substances. In order to investigate the true nature of the oscillations which give rise to these lines, the Raman spectra of a few organic and inorganic subs-tances were previously investigated in this laboratory at different temperatures including that of liquid oxygen and it was observed that in some cases besides the appearance of the new lines mentioned above, some changes take place also in the properties of some of the Raman lines due to intramolecular vibration in single molecules at the low temperature. As for instance, in the case of chloro-form it was observed[2] that the twofold degenerate line 262 cm^{-1} is split up into two equally intense lines at 263 cm^{-1} and 270 cm^{-1} respectively at the low tem-

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* Read before the Indian Physical Society on the 18th December, 1936,

perature, and also in the case of the H₂S molecule the angle between the two S-H bonds was found[3] to be changed from 90° to about 108° in the solid state at the low temperature. In order to investigate whether the new lines with small values of $\Delta\nu$ appear invariably in the case of all substances in the solid state and whether other molecules having high elements of symmetry are deformed to some extent at the low temperature, the Raman spectra of the three substances, phosphorus trichloride, cyclohexane and chlorobenzene, representing three different types of molecules, have been studied in the solid state at low temperature in the present investigation, and the results are discussed in the present paper.

EXPERIMENTAL.

The liquids used were pure and the purity was tested in each case by recording the Raman spectrum at the room temperature in the liquid state. The experimental arrangements were the same as used in this laboratory in the previous investigations mentioned above. Liquid oxygen was contained in a transparent Dewar vessel and in each case a pyrex tube containing the liquid was kept immersed in the liquid oxygen and in this condition the Raman spectrum of the solid was photographed. In the case of cyclohexane, the Raman spectrum was photographed also at the temperature of liquid ammonia in order to ascertain whether some changes observed at the temperature of liquid oxygen were due to change of state or of temperature. The spectrum of iron arc was photographed on each spectrogram and was used as comparison.

RESULTS AND DISCUSSION.

Phosphorus trichloride.

It was found on carefully examining the spectrogram due to solid phosphorus trichloride that inspite of the fairly large densities of the Raman lines due to intramolecular vibrations, not a single new Raman line appears in the neighbourhood of the Rayleigh line in the case of solid phosphorus trichloride at the low temperature. The significance of this fact will be discussed in the sequel. The lines observed in this case at the two temperatures are listed in table I, in which the figures in parentheses indicate the intensities estimated roughly from visual examination of the densities.

TABLE I.

Phosphorus trichloride.

30°C, (liquid)	$\Delta\nu$ in cm⁻¹	190(4)	258(2)	484(2b)			511(2b)
-180°C, (solid)	,, ,, ,,	194(4s)	255(3)	461(1s)	476(2s)	482(1s)	494(4s)

It will be observed from the results given in table I that the line 190 cm^{-1} is slightly shifted towards the longer wave-length and the lines 484 cm^{-1} and 511 cm^{-1} are shifted towards the Rayleigh line and also two new sharp lines at 461 cm^{-1} and 482 cm^{-1} appear when the substance is solidified and cooled to the temperature of liquid oxygen. It is also observed that at the room temperature each of the lines 484 cm^{-1} and 511 cm^{-1} is very broad and in fact they touch each in a manner which indicates that there is a line lying between them. In order to explain the width of the lines 484 cm^{-1} and 511 cm^{-1} and the sharpness of these lines at the low temperature it is natural to assume that rotation of molecules is responsible for the width of the lines in the case of the liquid state, but a little closer examination of the spectrogram shows that such an explanation is not tenable. Each of the lines 484 cm^{-1} and 190 cm^{-1} is due to an oscillation which is twofold degenerate and the rotation of molecules will cause an widening of both the lines to the same extent. Hence due to rotation of molecules the line 484 cm^{-1} can be only as broad as the line 190 cm^{-1}, but actually it is thrice or four times so. Again the line 511 cm^{-1} being due to symmetric oscillation, rotation of the molecules cannot make it wide but can only produce an extremely feeble wing accompanying intense central line. Hence rotation of molecules alone cannot be responsible for the observed width of these two lines. An attempt may be made to find out whether the width is due to presence of isotopes of chlorine. It is well known that chlorine has two isotopic atoms of atomic weights 35 and 37, the abundance ratio being 3:1. Four different types of molecules, *viz.*, PCl_3^{35}, $PCl_2^{35}Cl^{37}$, $PCl^{35}Cl_2^{37}$ and PCl_3^{37} can be formed out of these two isotopic atoms of chlorine. The percentage of each type of molecule in the liquid can be calculated easily with the help of the theory of probability. Such calculations give the following results :

	%
PCl_3^{35}	42·2
$PCl_2^{35}Cl^{37}$	42·2
$PCl^{35}Cl_2^{37}$	14·06
PCl_3^{37}	1·54

The molecule being pyramidal, it has four modes of vibration, all active in the Raman effect. Two of these vibrations are symmetrical and each of the other two is twofold degenerate. From a knowledge of the factor of depolarisation of the Raman lines, the symmetric and degenerate vibrations can be easily identified and with the help of the values of frequencies of these vibrations, the constants of the molecule have been determined by Trumpy.[4] If ν_1 and ν_2

denote respectively the frequencies of the two symmetric vibrations and ν_3 and ν_4 those of the degenerate vibrations, the expressions for ν_1, ν_2, ν_3 and ν_4, according to Trumpy, are

$$\nu_{2}^{1} = \frac{1}{2\pi} \sqrt{\frac{A \pm \sqrt{A^2 - \frac{12\alpha\beta}{\mu}}}{2p}} \qquad \ldots \text{(1)}$$

and

$$\nu_{4}^{3} = \frac{1}{2\pi} \sqrt{\frac{B \pm \sqrt{B^2 - \frac{\alpha(1 + 6\mu\beta)}{\mu}}}{2p}} \qquad \ldots \text{(2)}$$

where

$$A = 3a + \frac{1}{3} + \frac{\beta}{\mu} \quad , \quad B = \frac{3\alpha}{2} + \frac{1}{6} + \frac{1 + 6\mu\beta}{6\mu}$$

$$\beta = \frac{b^2}{a^2} \quad , \quad \alpha = \frac{K}{K'}\left(\frac{3\beta + 1}{3}\right) ,$$

$$p = \frac{m(3\beta + 1)}{3K'} ,$$

a is the normal distance between the chlorine atoms from one another, b is the perpendicular distance of the phosphorus atom from the plane of the chlorine atoms, m is the mass of the chlorine atom and $\mu = M/(M + 3m)$, M being the mass of the phophorus atom. As will be shown in the sequel, in the solid state the constants of the molecule become a little different from those in the liquid state. Taking ν_1 for $PCl_3{}^{35}$ as 494 cm^{-1} and with the constants for the solid state, ν'_1 for $PCl_3{}^{37}$ becomes 488 cm^{-1}. Hence this line due to ν_1 of $PCl_3{}^{37}$ molecule ought to be 6 cm^{-1} away from the line 494 cm^{-1} and the corresponding lines due to $PCl_2{}^{35}Cl^{37}$ and $PCl^{35}Cl_2{}^{37}$ ought to lie between these two lines at distances 2 cm^{-1} and 4 cm^{-1} respectively from the line 494 cm^{-1}. Since the percentage of $PCl_3{}^{37}$ molecules is negligible and that of $PCl^{35}Cl_2{}^{37}$ is only about 14%, only an extra intense line at about 492 cm^{-1} is expected in the solid state due to the presence of the isotope Cl^{37}, and the maximum width of the line due to this cause may be only about 4 cm^{-1}. It can be easily seen therefore, that the presence of the isotopic molecules can neither explain the observed width of the line 511 cm^{-1} in the case of the liquid nor can it explain the appearance of two new lines at 461 cm^{-1} and 482 cm^{-1} in the solid state at the low temperature. The observed width of the line 511 cm^{-1} seems to be due to transitions from the excited states corresponding to the vibrations ν_2 and ν_4.

The relative intensities of the lines 461 cm^{-1} and 476 cm^{-1} are not equal, but are roughly in the ratio 1:2 and therefore they cannot be due to the simple,

splitting up of the degeneracy of the line v_3. Again, it might be thought probable that the lines 461 cm^{-1} and 482 cm^{-1} owe their origin to effect of anharmonicity of the vibrations so that they might be produced by transitions from the excited state of the vibration v_2 to those of the combined vibrations $v_2 + v_1$ and $v_2 + v_3$, but the ratio of the population of the excited state of v_2 to that of the ground state is only about 0˙55 : 1 at the temperature of liquid oxygen and this is too small to account for the observed intensity of the lines 461 cm^{-1} and 482 cm^{-1}. Hence the only probable explanation regarding the origin of these lines seems to be that the influence of crystalline field on the frequency v_3 is appreciable and this being different in the three different directions, gives rise to three different frequencies, two being of equal intensities and third lying between these two being a little more intense.

The constants of the molecule in the liquid state as given by Trumpy in table I of his paper mentioned above, give on actual calculation the values of v_1, v_2 and v_3 slightly different from those which he has given in the same table as calculated frequencies. The values of the constants which fit in with the observed frequencies have been found out by trial in the case of the liquid state, and by solving the equations for α and β in the case of the solid state. These values have been given in table II below.

TABLE II.

PCl$_3$

	$\dfrac{b^2}{a^2}$	K$' \times 10^4$.	K $\times 10^4$.	v_n calc in cm^{-1}	v_n observed in cm^{-1}.	% error.
Liquid	0˙2	20˙1	7˙5	$v_4 = 208$	$v_4 = 190$	9˙4
				$v_2 = 256$	$v_2 = 258$	0˙8
				$v_3 = 456$	$v_3 = 485$	6˙0
				$v_1 = 510$	$v_1 = 511$	0˙2
Solid	0˙16	18˙88	8˙12	$v_4 = 214$	$v_4 = 194$	10˙3
				$v_2 = 251$	$v_2 = 255$	1˙6
				$v_3 = 454$	$v_3 = 476$	4˙9
				$v_1 = 494$	$v_1 = 494$	0˙0

It will be seen from table II that the values of both $\dfrac{b}{a}$ and $\dfrac{K}{K'}$ have changed in the solid state at the low temperature.

Cyclohexane.

Just as in the case of solid phosphorus trichloride, no new Raman line was observed in the neighbourhood of the Rayleigh line in the spectrogram due to solid cyclohexane at the low temperature, although almost all the prominent lines of the cyclohexane molecule were recorded with moderate densities. This is significant in view of the fact that this molecule contains six carbon atoms forming a closed ring like the benzene molecule and the only difference between the shapes of the two molecules is that the latter one has a plane structure while the former has a puckered structure, and therefore, if the new lines in the neighbourhood of the Rayleigh line observed in the case of solid benzene be due to lattice oscillations, they ought to have been observed in the case of solid cyclohexane also. The absence of these lines in the latter case probably indicates that these lines are not due to lattice oscillations. This point will be discussed in more detail in the sequel.

The spectrogram due to solid cyclohexane at the low temperature was compared with those due to liquid cyclohexane at the room temperature and at about 200°C. The spectrogram at the high temperature was recorded by one of the present authors (S. C. S.) in collaboration with Mr. B. B. Maiti last year. It was found that at the low temperature the line 1266 cm^{-1} observed at the room temperature is split up into two lines at 1258 cm^{-1} and 1273 cm^{-1}; also the line 2921 cm^{-1} becomes about twice as broad as the line 2936 cm^{-1}. The spectrogram due to the liquid at the high temperature shows that the lines 425 cm^{-1}, 1028 cm^{-1}, 1266 cm^{-1} and 1442 cm^{-1} and 2921 cm^{-1} become very much broader at the high temperature than at the room temperature. Kohlrausch and Stockmair [5] have concluded from a comparison of the Raman spectra of cyclohexane with those of its monoderivatives that since the number of lines below 1500 cm^{-1} is much less in the case of cyclohexane than in the case of its monoderivatives, some of the lines must be twofold degenerate and the probable symmetry of the molecule should be S_{6u}. For this symmetry of the molecule, there ought to be four twofold degenerate vibrations having frequencies less than 1500 cm^{-1}. These vibrations have been identified by them with the lines 425^{-1}, 1028 cm^{-1}, 1266 cm^{-1}, and 1442 cm^{-1}. The values of ρ, the factor of depolarisation, of the degenerate vibrations ought to be $6/7$ but the value of ρ for the line 1266 cm^{-1} reported by Cabannes, and Rousset,[6] is 0·7. Hence there might be some doubt regarding the twofold degeneracy of the line 1266 cm^{-1}, but since this line is observed to be split up into two equally intense components at the low temperature, the twofold degeneracy of the line is established beyond doubt, and therefore the probable symmetry of the molecule is S_{6u}, *i.e.*, the molecule has the " chair " form as pointed out by Kohlrausch and Stockmair. Of the other three degenerate lines in the spectrogram for the solid, 425 cm^{-1} was very feeble, 1026 cm^{-1} was not split up and

the line 1442 cm^{-1} was found to be broadened a little. All these lines are widened very much at the high temperature. Again the line 2921 cm^{-1} was found to be a little broader at the low temperature than the line 2936 cm^{-1}. This is probably due to the effect of the crystalline field on the antisymmetric vibration of the CH$_2$ group, because this line has its origin in that vibration. The spectrogram due to solid cyclohexane at the temperature of liquid ammonia showed that the line 1266 cm^{-1} was not split into two. Hence this splitting is an effect of the lowering of temperature still further.

Chlorobenzene.

In the case of solid chlorobenzene at the temperature of liquid oxygen, the lines of the single molecule are observed to remain unchanged, but besides these lines, four new Raman lines appear with $\Delta\nu$ in wave numbers respectively equal to 49 (2), 67 (1), 86 (1) and 103 (2s). The intensities of these new lines are of the same order of magnitude as those of the prominent Raman lines of the single molecule. These new lines as well as those observed previously in the case of p-dichlorobenzene and p-dibromobenzene at the temperature of liquid oxygen are listed in table III for comparison.

<div align="center">

TABLE III.

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Chlorobenzene	$\Delta\nu$ in cm^{-1}	49 (2), 67 (1),	86 (1)	105 (2s)
p-Dichlorobenzene	,, ,,	55 (2) 60 (2)	—	105 (2s)
p-Dibromobenzene	,, ,,	42 (3) —	—	104 (2s)

Table III shows that the line 105 cm^{-1} is present in the Raman spectra of all the three substances at the temperature of liquid air. According to the theory of lattice oscillation however, $\nu \propto \sqrt{\dfrac{T_s}{Mv^{2/3}}}$ where T$_s$ is the melting point, v the grammolecular volume, M is the molecular weight and ν the frequency of oscillation of the lattice. If by virtue of this relation one of the frequencies be coincident in a number of cases, the other frequencies also should be so.

The above fact, therefore, can not be reconciled with the hypothesis that these lines are due to lattice oscillations. Such a hypothesis was originally put forward by Gross and Vuks [1] and later, Vuks [7] supported it by studying the Raman spectra of different modifications of p-dichlorobenzene. Recently, Venkateswaran [8] has studied the Raman spectra of phosphorus and sulphur and has interpreted the results obtained by him with the help of the same hypothesis. Since Venkateswaran has remarked that the previous works of one of the present authors, [9] in which it has been shown that the shifts of these lines observed in some cases with the lowering of temperature of the crystals do not agree with

those calculated from the theory of lattice oscillations, have little significance, we shall discuss here in detail, how far these remarks are justifiable and how far the theory of lattice oscillation is able to interpret the observed facts.

Venkateswaran has raised the objection that Lindemann's formula cannot be used in the case of a lattice other than cubic. In stating so he seems to have confused with each other the different formulae for the frequency of lattice oscillations. It is the formula derived by Born [10] from dynamical considerations, which cannot be applied in the case of a crystal other than cubic, because a solution for the equations of motion can be obtained only in the case of regular diagonal lattice derived from a cubic lattice of NaCl type. The fomula

$$\nu = C \times 0.77 \times 10^{12} \sqrt{\frac{T_s}{Mv^{2/3}}} \qquad (i)$$

was, however, derived by Einstein [11] from considerations of dimensions and Lindemann [12] found the value 2.12 for the value of C in this formula. There is no such strict restriction for the applicability of this formula in the case of different crystal systems as Born's formula, but it is true that Einstein's formula is applicable only in the case of atomic lattices and cannot be applied direct in the case of molecular lattices in which different atoms in any molecule are again vibrating against each other. Braunbek, [13] however, deduced the following formula for the smallest frequency of oscillation of any lattice from considerations of the kinetics of melting of a substance :

$$\nu = \left\{ \frac{1}{2\chi} \left(\sqrt{\frac{M_1}{M_2}} + \sqrt{\frac{M_2}{M_1}} \right) \sqrt{\frac{3nR}{0.31}} \times L^{\frac{1}{3}} \right\} \sqrt{\frac{T_s}{Mv^{2/3}}} \qquad \dots \quad (ii)$$

where T_s, M and v denote as in formula (i), the melting point, molecular weight and gram-molecular volume respectively. M_1 and M_2 are the weights of the two kinds of atoms in the molecule, which build up the two lattices vibrating against each other, n = number of atoms in the molecule, R is the gas constant, L is the Loschmidt's number, and

$$\chi = s \left(\frac{L}{v} \right)^{\frac{1}{3}}$$

s being the primitive translation of the lattice in the direction in which the oscillation takes place for the smallest frequency.

Assuming v to be equal to Nd^3, N being Avogadro's number,

$$\chi = \left(\frac{L}{N} \right)^{\frac{1}{3}} \cdot \frac{s}{d} \qquad \dots \quad (iii)$$

Since $\dfrac{s}{d}$ remains constant at all temperatures, for the purpose investigating

the values of v of a particular lattice at different temperatures, formula (li) reduces to

$$v = k \sqrt{\frac{T_s}{Mv^{2/3}}} \qquad \qquad ... \ (iv)$$

which is exactly of the same form as Einstein's formula. This formula can be applied to any crystal system but k has different values for different systems and for different substances. As one of the authors [9] applied a formula of the same form as formula (iv) for calculating the changes in molecular volumes of any particular substance from the observed changes in v caused by change of temperature of the crystal, the objection raised by Venkateswaran is not justifiable. The value of k can be evaluated for any particular substance and the absolute value of v can be found out. Braunbek[13] has done this in the case of crystals of KCl, KBr, KI, NaCl, and AgBr, and the calculated values agree fairly well with the observed "reststrahlen" frequencies, the maximum discrepancy being 7%. From this fact it is evident that formula (iv) can explain facts as satisfactorily as Lindemann's formula, but in Lindemann's formula, k is assumed to be constant for different substances while it is not so in the case of formula (iv). But, as has already been said, since in formula (iv) k remains constant for a particular substance for different temperatures and Lindemann's formula can be applied only in the case of an atomic lattice the results obtained by one of the authors[9] previously by applying formula (iv) have much more significance than those obtained by Venkateswaran by applying Lindemann's formula with 2·75 as the value of C in the case of the molecular lattice of phosphorus.

There is, however, another criterion to judge whether the new lines which appear in the case of solids in the neighbourhood of Rayleigh lines are due to lattice oscillations or not. It is well known that the intensity of the Raman line due to any mode of vibration gives a direct measure of the change in polarisability of the vibrating unit, which takes place during the transition from the lower vibrational state to the higher one. If we consider the case of solid carbon disulphide studied previously by one of the present authors,[2] we see that the new line 70 cm^{-1} observed at the low temperature is almost three times as intense as the line 655 cm^{-1} due to symmetric vibration of the CS_2 molecule. It is well known that the change in polarisability in the case of the symmetric oscillation is the greatest of all such changes which can occur during any mode of vibration of the molecule. If it be assumed that the line 70 cm^{-1} is due to lattice oscillation, it leads to the conclusion that the polarisability of the CS_2 molecule itself changes by greater amount with the approach of another CS_2 molecule near it than in the case of the symmetric oscillation of the CS_2 molecule itself. This is highly improbable in the case of a non-polar molecule like CS_2. As has already been stated, no new lines appear in the neighbourhood of the Rayleigh line in the case of solid phosphorus trichloride, and therefore even in the case of the polar mole-

cule of PCl_3, the polarisability does not change considerably with the approach of another PCl_3 molecule near it. On the other hand if it is assumed that a new electronic binding occurs in the solid state between two CS_2 molecules resulting in the formation of a polymerised group, the strength of the binding will change very much with the change in the distance of the two constituent molecules in each such group during the vibration of one CS_2 molecule against the other and thereby a change in polarisability will be produced which may be much greater than that occurring during the symmetric vibration of the CS_2 molecule itself. Hence, as has been pointed out in previous communications, the observed high intensities of the new lines also leads to the conclusion that these lines are due to vibrations in polymerised groups. The dependence of the positions of these lines on the nature of the lattice has been discussed by the present authors very recently.[14]

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STUDIES ON SOME INDIAN VEGETABLE OILS, PART IV

Absorption of Air.

BY G. N. BHATTACHARYYA, M.Sc.

(Ghose Research Scholar in Applied Physics.)

ABSTRACT. The absorption of air by six Indian vegetable oils, *viz.*, Groundnut, Olive, Sesame, Chaulmoogra, Indian Rape and Indian Kapok, has been measured at the room temperature by a manometric method. It is found that the values of the Bunsen absorption coefficient for these oils are of the same order of magnitude as those of the mineral oils.

INTRODUCTION.

In the previous communications [1] the author reported the results obtained on the viscous and dielectric properties of a number of Indian vegetable oils. The object of the present paper is to measure the absorption of air by these oils at the room temperature.

Until recently the determination of the absorption coefficient for air and other gases had been mainly confined to inorganic and organic liquids whose compositions are definitely determinable. In view of the complex nature of the oils in general, very little progress was made in obtaining corresponding data in these cases, although such a study is necessary for ascertaining their suitability as insulators in electrotechnics.

During the last few years, however, considerable amount of work has been done in determining the absorption of air by mineral oils. These results have explained the anomalous behaviour of insulating oils in many cases. The anomaly which was observed in the dielectric strength of these oils at different temperatures has been attributed by Clark [2] to the absorption of air in different amounts. Very recently Gemant [3] has also measured the absorption coefficient and its temperature sensitivity for a number of mineral oils. No such data are yet available in the case of the vegetable oils. It was therefore thought of interest to undertake this investigation.

THEORETICAL CONSIDERATIONS.

The Bunsen absorption coefficient is the volume of the gas (reduced to normal pressure and 0°C.) absorbed by 1 c.c. of the liquid at a partial pressure

of 760 mm. of mercury. In the case of liquids obeying Henry's law this is determined at room temperature from the relation

$$a = \frac{T_0}{T} \cdot \frac{V}{v}$$

where a = the absorption co-efficient,

T = the absolute temperature of the gas,

T_0 = the absolute temperature corresponding
to $0°C. = 273°.1$,

V = volume of the gas absorbed,

and v = volume of the liquid.

It is evident from the above that when the absorption coefficient is measured at the room temperature, it is quite unaffected by the vapour pressure of the liquid as shown below.

The volume of the absorbed gas at a partial pressure of $(P-p)$ when reduced to normal pressure and temperature is

$$V \left(\frac{T_0}{T} \cdot \frac{P-p}{P_0} \right)$$

where P_0 = normal atmospheric pressure = 760 mm.
of mercury,

P = ordinary atmospheric pressure,

p = vapour pressure of the liquid at the absolute
temperature T.

But according to the definition of the Bunsen absorption coefficient, the volume should be found at the partial pressure of 760 mm. of mercury. Hence applying Henry's law, we have

$$a = \frac{V}{v} \left(\frac{T_0}{T} \cdot \frac{P-p}{P_0} \right) \cdot \frac{P_0}{P-p}$$

$$= \frac{T_0}{T} \cdot \frac{V}{v},$$

which is identical with the relation given before

EXPERIMENTAL.

A manometric method has been used for the determination of the absorption coefficient of the oils at the room temperature. A diagrammatic sketch of the arrangement is shown in figure 1. The manometer has been designed in the
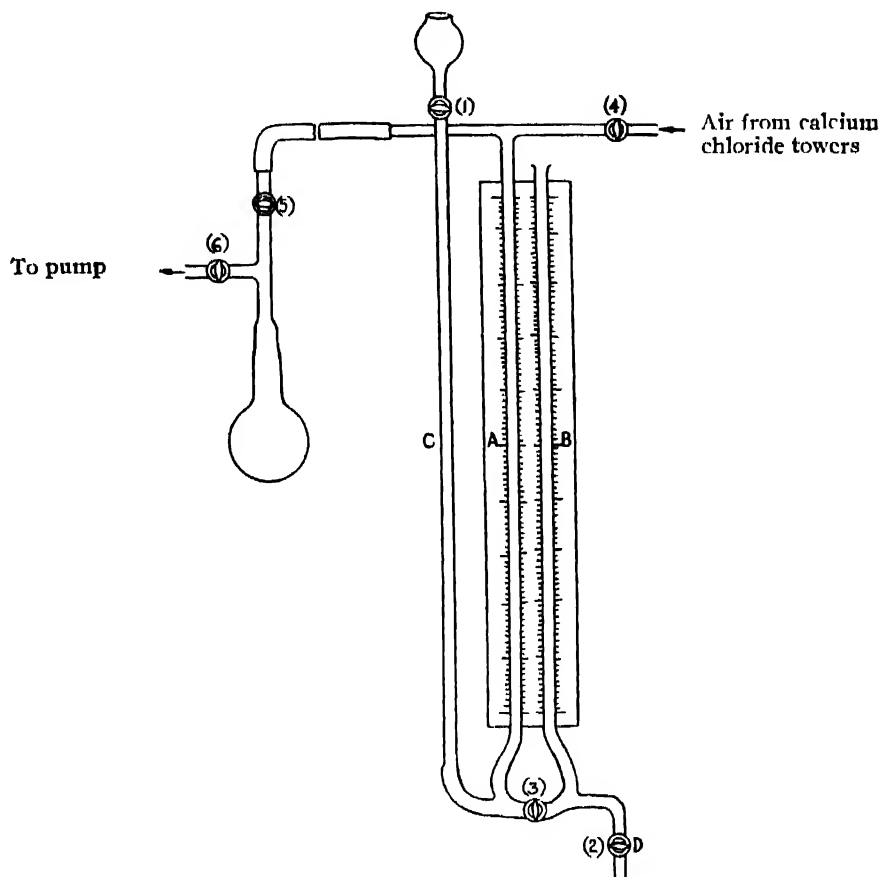
FIGURE 1.

Diagrammatic sketch of the arrangement.

laboratory. It is constructed of a glass tube of about 4 mm. diameter with the two limbs, A and B, placed very close to each other so as to facilitate a comparison of the readings of their mercury menisci. A millimetre scale is fixed vertically behind these limbs. The long capillary tube, C, with a stop-cock, T_1, and a mercury reservoir, R, is joined to the base of the manometer in order to transfer mercury from the reservoir to the limbs. By means of the outlet tube D, having a stop-cock T_2, mercury can, however, be removed from the manometer. The flow of mercury from one limb to the other can be stopped by means of the stop-cock T_3. The gross height of the manometer is about 85 cms., while the working length of each of the limbs is nearly 60 cms.

The limbs of the manometer have been calibrated as follows: They were first filled with pure mercury avoiding the presence of air bubbles inside them, and the readings of the mercury menisci noted by means of a low range telescope. A quantity of it was then taken out through the outlet tube D, and weighed. From the difference of the initial and the final readings of the mercury menisci and from the density of the mercury at the room temperature the volume per unit length of the manometric tube was determined.

The method of procedure consisted in degassing first a definite volume of the oil under investigation and in then ascertaining the volume of air absorbed by it at the temperature of the room. For degassing, the method employed by Gemant was adopted. The oil was enclosed in a 150 c.c. flask provided with a side tube and a stop-cock, T_6, and having its neck drawn out and fitted with another stop-cock, T_5, for connecting it with the manometer. The flask was connected with a shaking device (not shown in the figure) worked by means of an electric motor, so that the oil inside it could be given a continuous shaking. Under this condition degassing of the oil was secured by subjecting it to evaquation by means of a Gaede oil pump, connected to the side tube of the flask. At first profuse bubbles of air came out. Their rate of evolution however diminished very rapidly. It was found by a series of trial observations that the oils under investigation were completely degassed after they were subjected to simultaneous shaking and evacuation for about an hour and a half. In practice the above procedure was continued for a still longer period (3 to 4 hrs.) with a view to eliminate the risk of having an incomplete degassing. It was, however, generally found that the thinner oils are degassed more quickly than the thicker ones.

When the process of degassing was completed, the flask was brought to rest and the stop-cocks T_5 and T_6 were closed. The stop-cock, T_4, was then opened to introduce dry air (obtained by passing atmospheric air through calcium chloride towers) into the tubes connecting the flask with the manometer. Some time was allowed for eliminating the error which might arise due to the absorption of air by the rubber tubings. By opening the stop-cock, T_5, dry air was next admitted slowly at the atmospheric pressure into the flask. The stop-cock, T_4, was then quickly closed, and the connection with the manometer established by opening the stop-cock, T_3. It was however noticed that the absorption process was extremely slow and required a long time when the oil was kept at rest. But if it was subjected to shaking, the absorption process was completed within about half-an-hour. Due to the absorption of the enclosed air by the oil, the pressure inside the flask fell as was shown by the rise of the mercury meniscus in the enclosed limb, A, of the manometer. Mercury was then transferred from the reservoir, R, to the manometer until the mercury menisci were again at the same level. The difference in the readings of their original and final levels gave directly the volume of air absorbed by the oil.

Adopting the above procedure six Indian vegetable oils were examined. None of them belonged to the category of a drying oil. Some of their characteristic physical data so far obtained by the author are given in table II. For each oil about 50 c.c. was taken. The exact volume was, however, ascertained from a knowledge of its mass and density. These results are given in table III which also includes the values of the absorption coefficients of air by the oils investigated.

It may here be noted that before making any observations on the oils under investigation, the accuracy obtainable with the apparatus and the method used was ascertained by measuring the absorption of air by a few liquids for which such data are available. Results of such measurements in the case of water and transformer oil at the room temperature are included in table I. It will be seen that they are in good agreement with the existing data.

RESULTS.

Vol. per cm. of the tube = 0·16484 c.c.

TABLE I.

Test Measurements.

Liquid.	Room temp. in °C.	Vol of liquid taken (c.c.).	Rise of mercury (cms.).	Absorbed Vol. of air (c.c.).	Absorption coefficient (calculated).	Absorption coefficient (Literature).
Water	23·1	75·0	9·1	1·500	·01832	·01769[5]
,,	22·3	95·0	11·7	1·929	·01871	·01801[5]
Transformer Oil (Vac. Oil Co.) B. S. grade —A 30	22·1	50·2	31·3	5·159	·09512	·09200[3]

TABLE II.

Characteristic Physical Data.

Oil.	Density.	Refractive index.	Viscosity in secs. (Red-wood) at 23°.9C.
Groundnut	0·9111 (21°·3C)	1·4621 (33°C)	274·3
Olive	0·9107 (20°·7C)	1·4672 (27°·8C)	294·5
Sesame	0·9177 (20°·5C)	1·4713 (27°·8C)	256·3
Chaulmoogra	0·9543 (22°·1C)	1·4770 (33°C)	766·0
Indian Rape	0·9078 (21°·3C)	1·4713 (24°·2C)	351·3
Indian Kapok	0·9232 (22°C)	1·4857 (33°C)	549·0

TABLE III.

Absorption Data.

Oil.	Room Temp. in °C.	Mass of oil taken (gms,).	Vol of oil (c.c.).	Rise of mercury (cms.).	Vol. of air absorbed (c.c.).	Absorption coefficient.
Groundnut	21·3	45·220	49·6	31·8	5·242	0·09806
Olive	20·7	44·720	49·1	30·5	5·028	0·09519
Sesame	20·5	44·650	48·7	25·4	4·187	0·07998
Chaulmoogra	22·1	46·710	49·0	27·5	4·533	0·08553
Indian Rape	21·3	44·470	49·0	30·0	4·945	0·09381
Indian Kapok	22·0	45·55	49.4	35·8	5·902	0·11060

DISCUSSION.

It has been stated in a previous section that the absorption of air by an oil takes place very slowly when the latter is kept at rest. This can be seen from the absorption-time curves, given in figures 2 and 3, for the Indian Kapok oil either when it is at rest or subjected to shaking. The reason for selecting this
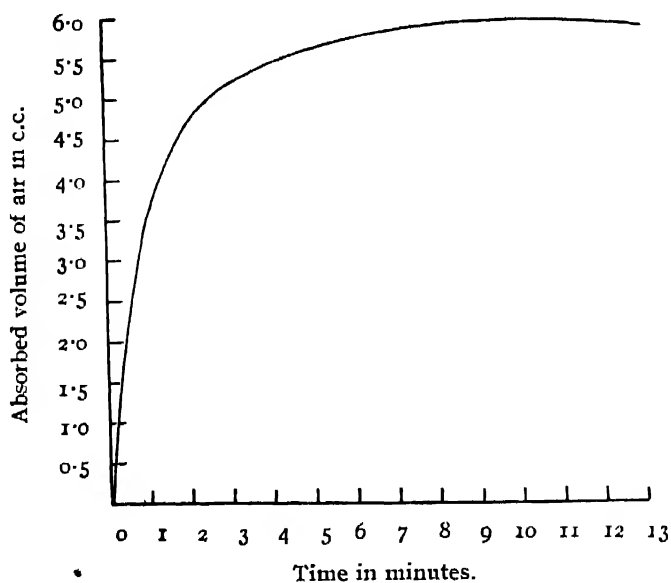
FIGURE 2.

Absorption-time curve of Indian Kapok oil, oil being shaken continuously.
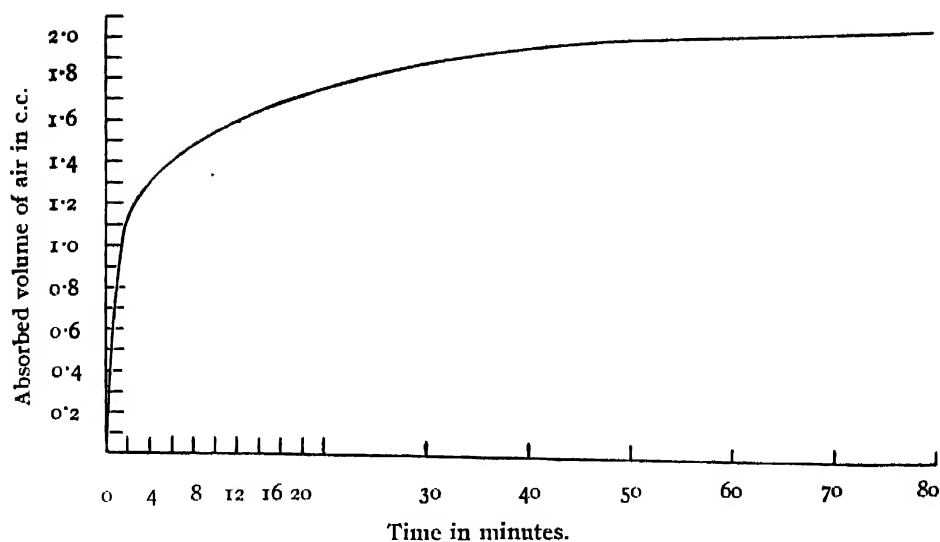
FIGURE 3.

Absorption-time curve of Indian Kapok oil, oil being at rest.

particular oil for illustrating the above effect is that the rate of absorption of air in this case is highest amongst the oils studied in the present investigation. The nature of these curves for the other oils is, however, similar, and may therefore be taken as typical for non-drying oils.

It may further be noted that the absorption-time curves for these oils when subjected to shaking resemble very much in nature to those of the mineral oils under identical conditions. On the other hand the nature of these curves when the oils are at rest does not show such an exact similarity. From the observations of Gemant[3] and Clark[4] it is found that in the case of the mineral oils at rest absorption takes place at an uniform rate for the first few hours, after which the rate diminishes. For the vegetable oils, however, the rate of absorption is very high for the first few minutes and then slows down.

One also notices that the values of the Bunsen absorption coefficient for the vegetable oils are of the same order of magnitude as those of the mineral oils.

It is proposed to take up in immediate future the measurement of the absorption of air by these oils at different ranges of temperatures and determine therefrom the temperature sensitivity of their absorption coefficients. The measurement of absorption of air by drying vegetable oils is in progress and will be reported in a separate communication.

The author acknowledges his best thanks to Prof. P. N. Ghosh who has given all facilities for carrying out the investigation and shown continued interest during the progress of the work.

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REVIEWS

THE ANNUAL TABLE OF CONSTANT AND NUMERICAL DATA

(Published by Institute de Chimie, Paris.)

These annual tables are well known and the three present volumes, namely, the Numerical data on Rotatory Power by Prof. E. Darmois and those on Radio-activity, Nuclear Physics, Transmutation, Neutrons and Positrons by Joliot-Curie, B. Grinberg Wallen of the Institute De Radium and on Raman Effect by Dr. M. Magat of the College de France form a definite contribution for reference purposes.

The first one on rotatory power deals with data published during 1931-34 and is divided into five sections, namely, the specific rotatory powers of various groups of substances in the homogeneous states and in solution. In this section one finds hydrocarbons, fatty acids, sugar and its derivatives, amino-acids, polypeptides, diphenyl derivatives, terpenes, alkaloids and miscellaneous bases.

The second section is on the effect of temperature, concentration and solvent on rotatory power. Here one finds data regarding cellulose and starch as well as on vitamine D.

The third section deals with rotatory dispersions. Here one finds the new data of ascorbic acids, besides the data on various well known substances. The fourth section is on the revolution of racinic compounds and the fifth on muta-rotation.

The sixth section is about the effect of addition of esters, tartarates, sugars and other miscellaneous compounds.

The seventh section is about general theories such as Walden inversion, optical superposition, and asymmetric synthesis.

The second one on radio-activity and allied subjects comprises data from 1931 to April, 1936. Here one finds the section on radio active bodies, their half lives, α-rays, β-rays, γ-rays, radio-activity of potassium and of the rare earths, the heat evolved during radio-active transformation, chemical effects of radiations and the radio-activities of minerals and spring waters.

The third one on the Raman Effect is in continuation of a similar one published earlier in which data up to 1931 were included, and the present one deals with results published up to 1934. Though it is not up-to-date, it is very useful o research workers because it includes not only the Raman frequencies of the substances studied during the period from 1931 to 1934 but also gives the values of the factors of depolarisation of the lines wherever these values are available. The table is divided into three sections—Inorganic, Organic and the last section, which is theoretical, deals with different modes of vibration of polyatomic molecules and includes diagrams of such modes of vibration.

10

THE STRUCTURE OF METALS AND ALLOYS

By

WILLIAM HUME-ROTHERY, M.A., D.Sc.

(The Institute of Metals, 3s. 6d.)

Dr. Hume-Rothery is very well known to the investigators of metallic alloys as expounder of varying electronic valency of metallic elements in the formation of alloy system. As stated in the preface the monograph is written at the request of the Council of the Institute of Metals. Within the last two decades large amount of informations has been collected and it has been indeed difficult for any worker to secure the informations in a single treatise.

The book is divided into five parts. Part I deals with the electronic background to metallurgy, starting from the structure of the atom developing that of the molecule and finally dealing with the structure of the crystals. Parts II and III deal with the crystal structure of the elements and their atomic radii. Part IV gives a comprehensive survey of the primary metallic solid solutions, the pioneer work in this subject due to Bain, Onowen and Preston. The X-ray diffraction photographs has revealed the nature of crystal lattice and super-lattice and Dr. Hume-Rothery has himself contributed substantial work in this domain. The form of liquidus curves of several systems representing different types and the form of solidus curves as well as the lattice constants of some important alloys have been treated in this section. Part V deals with the intermediate phases in alloy systems. The question of the sharing of electrons in co-valent linkages of atoms and in ionic structures the passage of valency electrons from one atom to another with the production of oppositely charged ions has been the starting point. Number of typical structures have now been treated and finally the cases where structures are determined by the size factor. Part VI is a collection of work on imperfections in crystals—a subject which is comparatively undeveloped but undoubtedly of the greatest importance to metallurgy. Here, as the author has clearly stated, a knowledge of the ideal crystal structure as revealed by the ordinary X-ray crystal structure analysis is not sufficient and urges new methods of investigations.

Each section has a very complete bibliography upto 1935.

AN INTRODUCTION TO THE THEORY OF ELASTICITY

By

R. V. SOUTHWELL.

(Oxford Clarendon Press, 30 shillings).

This volume forms one of the Oxford Engineering Science series. Prof. Southwell has clearly laid down how in recent years a knowledge of the elastic properties of materials has been of growing importance to the Engineers. From the purely theoretical standpoint the classical treatise of the Mathematical theory of Elasticity by Prof. Love and treatment of problems concerning Elastic Vibrations by Lord Rayleigh in his Theory of Sound form the essential foundation on which the superstructure has constantly been added. For the Engineering students the above-mentioned treatises cannot be stated to be easy reading.

In the first three sections the basic relations of elastic bodies have been very clearly dealt with. The theorem of minimum strain energy and the principle of Saint-Venant have been discussed. In Section IV and V one finds discussion of the elementary theory of stress and strain, that of elastic failures and some typical cases of stress distribution has been worked out. Here one finds examples on beams of re-inforced concrete presented to a student. Sections VI and VII deal with deflection of girders. The normal vibrations of rods of uniform cross sections and beams resting on elastic foundation have been worked out. The theories of flexure and torsion as exemplified in bent plates helical springs and crank shafts are dealt with in this section. Sections VIII, IX and X really form the fundamental mathematical background. In Chapter XI one finds the solutions of the general equations as delineated in the last section. The gravitational stresses and the modification of stress due to thermal influences have suitably been introduced. The difficult problem of two dimensional stress systems has been taken up in the twelfth section. Sections XIII and XIV treat stability problems as arising out of the elastic properties of materials. The problem of critical load and its calculations follows the line adopted by Lord Rayleigh and finally the theory of vibrations as developed by Lord Rayleigh has been very clearly expressed. The book contains complete bibliographical and supplementary notes regarding the important treatises as well as original papers.

The book is really from the engineer's point of view, an excellent treatise where he will find his familiar applications treated from a rigid theoretical outlook.

SEMI-OPTICAL LINES IN THE X-RAY SPECTRA*

BY A. T. MAITRA, M.Sc. (PAT.)

(Government of Behar, Research Scholar.)

ABSTRACT. In this paper an attempt has been made to sort out some lines in the K, L, and M series of X-ray spectra which are somewhat different in character as regards their origin and have a peculiarity of their own. Such lines belonging to the K series are K_{β_1}, K_{β_3} and K_α; to the L series are L_α, L_{β_3}, L_{β_4}, L_{γ_1}, L_{γ_4}, &, L_{γ_6} and to the M series are M_{α_1}, and ($M_{III} \longleftarrow O_{IV}$), only for some particular elements in each of the series as mentioned in the paper. ν/R values of the final states of these lines have been shown to accord reasonably with those of the lines themselves. An attempt has, therefore, been made to bring out the analogy between the transitions of these lines with those of optical lines from the fact that a knocked out electron from an inner level of an atom goes to a vacant, partially vacant or optical level and then a transition from one of these levels gives rise to them. Hence the name ' semi-optical.' Also, available experimental facts have been put forward in support of the view adopted.

INTRODUCTION

The first idea of semi-optical lines in the X-ray region was developed by Backlin, Siegbahn and Thoraeus.[1] They plotted the wave-length difference between K_{α_1} ($K \rightleftharpoons L_{III}$) and K_{β_1} ($K \rightleftharpoons M_{III}$) against atomic number from Na (11) to Sc (21) and their curve began bending from S (16) and sloped down from Al (13) to Na (11). K_{β_1} is the transition from M_{III} level to K level. It has a faint component K_{β_3} ($K \rightleftharpoons M_{II}$) which is resolved for heavier elements beginning from Rb (37).

According to Stoner and Smith's model of electron structure of atoms, M_{II} level is completely filled up at Si (14) and M_{III} level at Ar (18). The M_{III} level begins to develop first from P (15). So the question of obtaining the K_{β_1} lines for Na (11), Mg (12), Al (13) and Si (14) becomes certainly curious. Similarly a plot of the wave-length difference between K_{β_1} and K_{β_5} ($K \longrightarrow M_{IV} M_V$) (a forbidden

transition and called K_{β_2} in the paper of the authors mentioned) against atomic number from K (19) to Cu (29) also showed an abrupt discontinuity of the curve at Sc (21) and it sloped down to K (19). There is no electron at all in $M_{IV}M_V$ level for K (19) and Ca (20). Thus the K_{β_1} lines for Na (11) to Si (14) and K_{β_5} lines from K (19) to Sc (21) were called semi-optical lines by the authors [1] mentioned above. Their idea was, that these lines were due to transitions of electrons from virtual optical levels. But an optical or virtual level must have an electron before it can serve as an initial state for the emission of a quantum. No further explanation for calling these K_{β_1} and K_{β_5} lines as semi-optical for the particular elements mentioned above was given.

A number of such semi-optical lines in the K, L, and M series of X-ray spectra have been selected and some possible explanations of their origin and the reason for calling them so have been attempted with the available experimental data.

SOME GENERAL CONSIDERATIONS AND DISCUSSION

An optical line of an atom originates, as we all know, when the valence electron of the atom is raised up to a higher virtual level or higher quantum state by the absorption of energy and then falls back to its initial level or some other level of lower quantum state, the transition being generally governed by the rules of selection. On the contrary, a true X-ray line arises when an electron from a particular inner level (say K) is knocked out of the atom by the absorption of energy, it being unable to go to other inner levels of the atom if these are completely filled up with their proper share of electrons, and another electron from some other filled up level jumps to the K level giving rise to a K emission line. The transition also in this case is governed by the rules of selection. Thus in the case of X-ray spectra the atom is first of all ionised in the inner level.

Now, let us call the last completely filled up level of an atom the periphery or the boundary of the atom. After the periphery lie the optical levels of the atom. Kossel's theory explained that the principal limit (say—, K or L) corresponds to the energy of transfer of an electron from the K or L level to the outside of the atom or to the first unoccupied orbit and the extended structure of the principal limit due to the transfer of the electron to the optical levels. But recently the theory of the extended structure of the principal limit has been modified by Kronig.[2]

That the main absorption limit or edge of an inner level of an atom might be due to the ejected electron from the inner level coming to rest in

the first unoccupied or partly occupied level, may be postulated if the energy

$\left(\text{or } \dfrac{\nu}{R}\right)$ value of the corrresponding emission line (the transition from the first

unoccupied or partly occupied level to the particular inner level) agrees with the main absorption limit of that particular inner level. In explaining the origin of the L_{II} and L_{III} principal limits for the elements Lu (71) to Au (79) Sandstrom [3] showed that the ν/R values of the L_{II} limits and L_{III} limits of those elements were equal to those of the L_{γ_6} [$L_{II} \rightleftharpoons O_{IV}$] and L_{β_5} [$L_{III} \rightleftharpoons O_{IV} O_V$] emission lines of the elements [Lu (71) to Au (79)] within the limits of experimental error. We must, therefore, infer that the emission of L_{β_5} or L_{γ_6} is exactly analogous to that of a resonance line in the optical region. L_{β_5} is due to the transition from $O_{IV} O_V$ to L_{III} level and L_{γ_6} is due to that from O_{IV} to L_{II} . But the O_{IV} , O_V levels are in a state of development from Yb (70) and are completely filled up with electrons at Au (79). So the knocked out electron from L_{II} or L_{III} level of each of these elements, instead of going beyond the periphery of the atom, goes to the O_{IV} or O_V levels. Then, these X-ray lines (having transition from O_{IV} or O_V to L_{II} or L_{III}) for the elements Lu (71) to Au (79) may, therefore, be called semi-optical lines. Similar is the case with L_{β_2} ($L_{III} \rightleftharpoons N_V$) and L_{γ_1} ($L_{II} \rightleftharpoons N_{IV}$) for the elements from Zr (40) to Ag (47), where the N_{IV} N_V levels are in a state of development and with L_{γ_4} ($L_I \rightleftharpoons O_{II} O_{III}$) from In (49) to Xe (54) where the $O_{II} O_{III}$ is also in a state of development. Detailed results for these are given below.

L Series :

Figure 1 is a plot of the wave-length difference between L_{α_1} ($L_{III} \rightleftharpoons M_V$) and L_{β_2} ($L_{III} \rightleftharpoons N_V$) against atomic number from (40) to (57).

The nature of this curve is similar to that of the wave-length difference between K_{α_1} ($K \rightleftharpoons L_{III}$) & K_{β_1} ($K \rightleftharpoons M_{III}$) against atomic number from (11) to (20) as shown by Backlin, Siegbahn and Thoraeus [1] mentioned in the earlier part of the paper. Figure 2 shows the same thing for L_{γ_1} ($L_{II} \rightleftharpoons N_{IV}$) when the wave-length difference between L_{β_1} ($L_{II} \rightleftharpoons M_{IV}$) and L_{γ_1} is plotted against the corresponding atomic numbers.

'A. T. Maitra

In explaining the origin of the L_{II} and L_{III} absorption limits of the elements [(70) to (79)] Sandstrom [3] has shown that the ν/R values of the L_{II} and L_{III} limits of these elements agree satisfactorily with those of L_{γ_6} and L_{β_5} as has already been mentioned. Kawata [4] has also experimentally shown that the L_{β_5} lines of W (74) and Pt (78) are strongly absorbed on passing through an
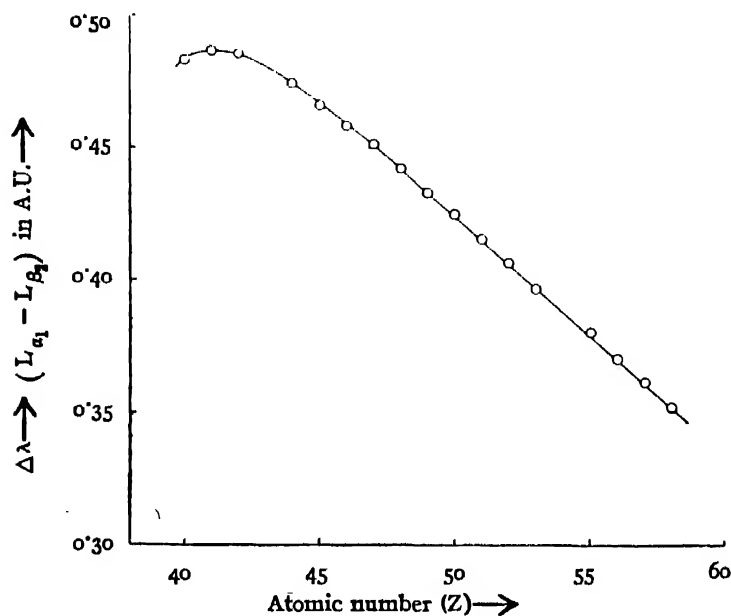
FIGURE 1.
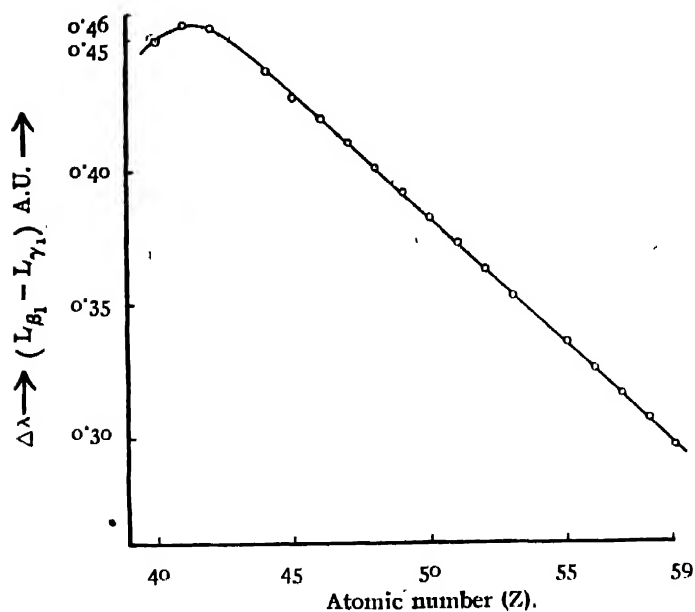
FIGURE 2.

absorption screen of W (74) and Pt (78). Figure 3 shows the relation between the difference between ν/R values of L_{III} and the ν/R values of L_{β_2} lines against atomic number. Figure 4 shows the same thing for L_{γ_1}.
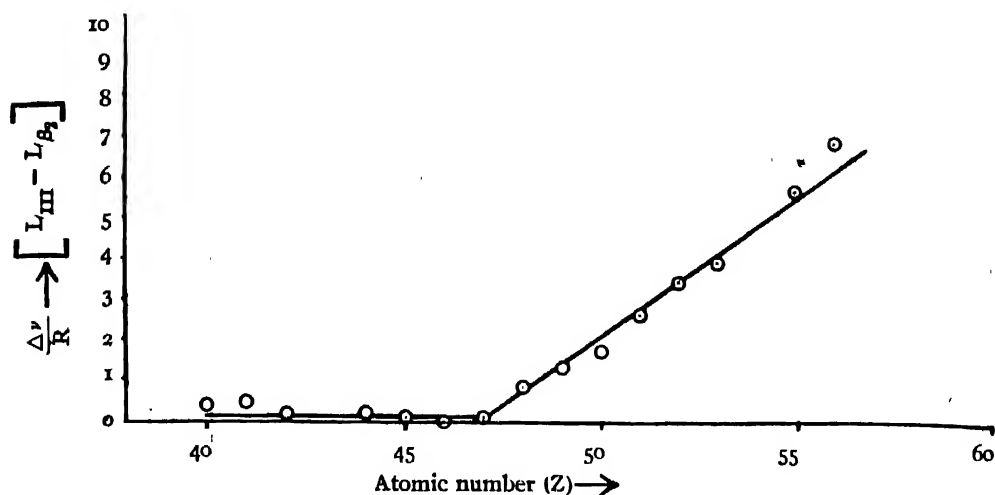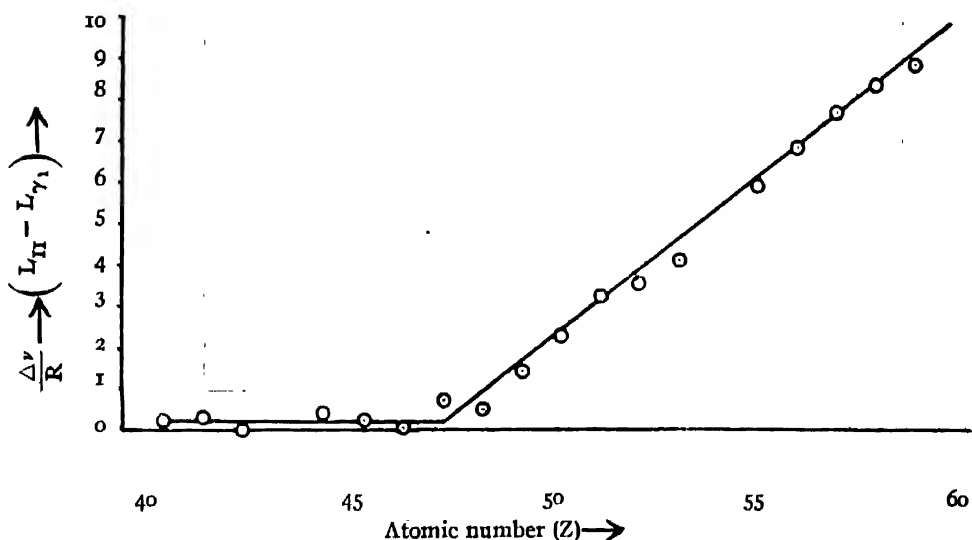
FIGURE 3.

FIGURE 4.

In tables I and II, are given these values for L_{β_5} from elements Lu (71), of L_{β_2} from Zr (40), of L_{γ_1} from Zr (40), of L_{γ_4} from In (49). In each of these cases the ν/R values of the principal limits agree with those of the corresponding lines within the limits of experimental error, for the elements whose particular levels, serving as initial states of the lines, are in a state of development. This means, say, as in the case of L_{β_5}, the knocked out electron from the L_{III} level of

any element beginning from Lu (71) to Au (79) goes to the $O_{IV} O_V$ level which is in a state of development for these elements.

TABLE I.

Atomic number (Z).	Number of electrons in O_{IV}, O_V level.	$\frac{\nu}{R}$ for L_{β_5} ($L_{III} \longrightarrow O_{IV} O_V$)	$\frac{\nu}{R}$ for L_{III}	Difference between L_{III} and L_{β_5}.	Remarks.
71	1		681·24		All experimental values, except where mentioned, are taken from Siegbahn's Spectroskopic Der Röntgenstrahlen, 2nd Ed., 1931.
72	2		704·77		
73	3	727·15	728·0	+ 0·85	
74	4	751·32	751·30	− 0·02	
75	5 or 6	775·75	775·21	− 0·54	
76	6 or 7	799·6	800·04	+ 0·44	
77	7 or 8	825·75	825·60	− 0·15	
78	9 or 10	851·48	850·89	− 0·59	
79	10	877·65	877·70	+ 0·05	Difference goes on increasing with atomic number as shown in Sandström's curves for L_{β_5} and L_{γ_6}.
80	10	905·21	904·53	− 0·68	
81	10	931·30	931·98	+ 0·68	

Atomic number.	Number of electrons in N_{IV} N_V level.	$\frac{\nu}{R}$ for L_{β_2} ($L_{III} \longleftarrow N_V$)	$\frac{\nu}{R}$ for L_{III}	Difference between L_{III} and L_{β_2}.	
40	2	163·48	163·87	+ 0·39	
41	4	174·37	174·84	+ 0·47	
42	5	185·59	185·81	+ 0·22	
43	6				
44	7	208·92	209·12	+ 0·20	
45	8	221·07	221·27	+ 0·20	
46	10	233·62	233·63	+ 0·01	
47	10	246·69	246·76	+ 0·07	Difference goes on increasing with (Z) as shown in Fig. 3.
48	10	259·89	260·71	+ 0·82	
49	10	273·56	274·85	+ 0·129	

<div align="center">TABLE II.</div>

Atomic number (Z).	Number of electrons in N_{IV}, N_V level.	$\dfrac{\nu}{R}$ for L_{γ_1} ($L_{II} \rightarrow N_{IV}$.)	$\dfrac{\nu}{R}$ for L_{II}.	Diff. between L_{II} and L_{γ_1}.	Remarks.
40	2	169·58	169·83	+0·25	
41	4	181·35	181·6*	+0·25	*These values are taken from Sommerfeld's Atomic structure and spectral lines (Vol I), Revised, 3rd Ed. (1934)
42	5	193·43*	193·39	−0·04	
44	7	218·38	218·8	+0·42	
45	8	231·53	231·79	+0·26	
45	10	245·19	245·28	+0·09	
47	10	259·15	259·91	+0·76	→Diff. goes on increasing with atomic number as shown in Fig 4.
48	10	273·81	274·33	+0·52	
49	10	288·81	290·26	+1·45	

Atomic number (Z).	NO. of electrons in O_{II}, O_{III} level.	$\dfrac{\nu}{R}$ for L_{γ_4} [$L_I \rightarrow O_{II}, O_{III}$].	$\dfrac{\nu}{R}$ for L_I.	Diff. between L_I and L_{γ_4}.	
49	1	312·17	312·14	−0·03	
50	2	328·82	329·03	+0·21	
51	3	346·02	346·27	+0·25	
52	4	363·68	363·94	+0·26	
53		381·89	382·26	+0·37	
54	6	...	401·02	...	
55	6	420·11	421·79	+1·68	Diff. goes on increasing with (Z).
56	6	439·91	441·9	+2·0	
57	6	460·54	462·85	+2·13	

The agreement between the ν/R values of the emitted and the absorbed quanta given in the above tables (I and II) seems to be fairly satisfactory if it is taken into consideration that the accuracy of the measurement of the absorption limits is not as good as that of the lines and that different values of the same limit are given by different experimenters.
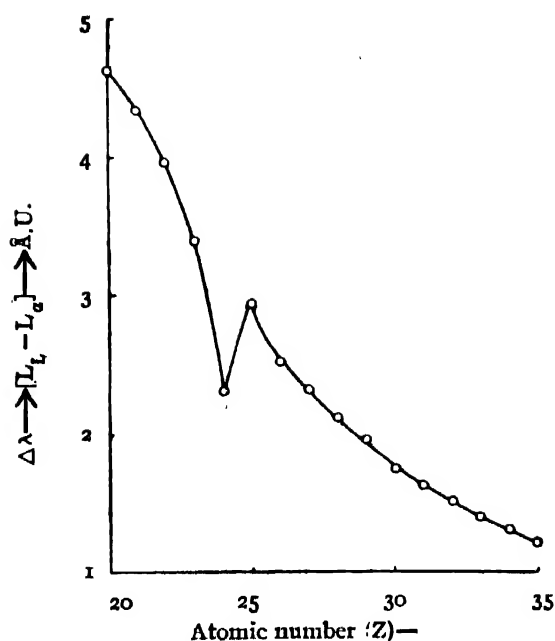
FIGURE 5.
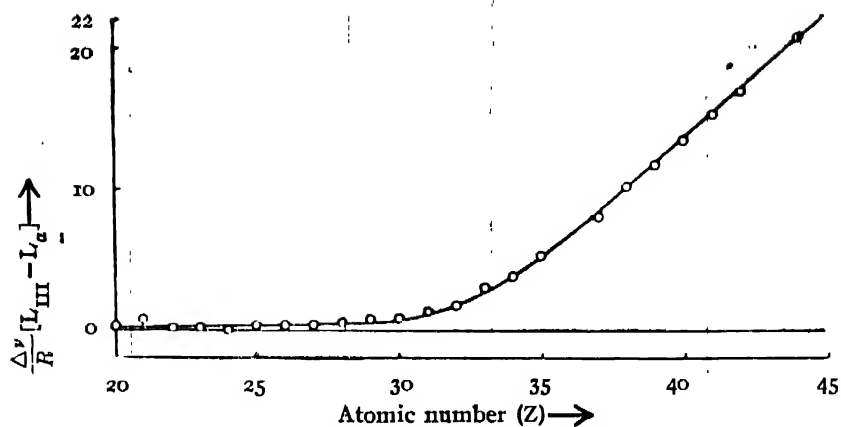
FIGURE 6.

Next, let us consider the L_a lines from $Ca(20)$ to elements of higher atomic number. Figure 5 shows a relation between the wave-length difference between L_l and L_a lines and atomic number. This curve is of surprising appearance and exhibits a marked discontinuity at $Cr(24)$. The relation between the difference between v/R values of L_{III} and L_a as a function of atomic number is shown in figure 6. In table III are given these values.

<center>TABLE III.</center>

Atomic number (Z).	Number of electrons in M_{IV}, M_V level.	$\frac{\nu}{R}$ of L_α [$L_{III} \longrightarrow M_{IV}\, M_V$].	$\frac{\nu}{R}$ of L_{III}.	Diff. between L_{III} and L_α.	Remarks.
20	...	25·2	25·59*	+ 0·39	* Prins and Taken's [5] experimental values of L_{II}, L_{III} for Ca(20) and Ti(22) and of L_{III} for Cu(29).
21	1	29·1	29·9	+ 0·8	
22	2	33·26	33·41*	+ 0·15	
23	3	37·7	37·9	+ 0·2	
24	5	42·3	42·3	0	
25	5	47·0	47·3	+ 0·3	
26	6	51·8	52·2	+ 0·4	
27	7	57·2	57·7	+ 0·5	
28	8	62·7	63·2	+ 0·5	
29	10	68·5	69·3*	+ 0·8	Diff. goes on increasing with (Z) as shown in Fig. 6.
30	10	74·51	75·4	+ 0·9	
31	10	80·86	82·18	+ 1·32	
32	10	87·50	89·3	+ 1·8	

In this case the experimental values[5] of L_{III} are only for Ca(20), Ti(22), and Cu(29). For other elements, besides these three, computed values of L_{III} are used from Siegbahn's Spectroskopie Der Röngenstrahlen (2nd. Ed., 1931). In the case of Ga(31), L_{III} has been computed from ($K - K\alpha_1$), where the experimental value of K given by Kievit and Lindsay [6] has been adopted. Their value of the K limit of Ga seems to be more correct than that of others as has been emphasised and experimentally verified very recently by Mutch. [7] From Rb(37) onwards the experimental values of L_{III} have been utilised. In the case of Ca and Ti the experimental values are of L_{II}, L_{III}; this means that actual values of L_{III} will be still less and, therefore, the agreement between the absorbed and emitted quantum may be expected to be still better.

On the whole, the agreement is not far from satisfactory if the widths of the emission lines in this region, are also taken into consideration. It would be quite interesting to photograph suitable absorption limits and the L_α lines in this region on the same photographic plate. It may be also possible that the L_{III} electrons, for the non-metals, instead of going to the first unoccupied or incompletely filled up orbit, goes to optical levels as has been also suggested by Mukerjee and Ray.[8] If this is so then the L_α lines for them are due to transitions from the optical levels to the L_{III} level. Therefore, the main point seems that these so-called semi-optical lines are due to transitions of electrons from that particular

2

level (may it be the first unoccupied or partly occupied orbit or an optical level, or conduction level) where the knocked out electron from the inner level, lodges itself.

Although the above view may hold good, as the agreement between the emitted and the absorbed quantum is quite good in some cases, there remains also a slight difference in some of them ; and this departure has, perhaps, got a significance like this. We should take into consideration that the experimental values of wave-lengths are obtained not from free atoms but from metallic crystals which according to Kroning [9] consist of permitted and forbidden energy zones of definite width. Also according to conduction theory of metals [10] the incomplete number of electrons in a level (valence level) of an atom, form the lower of the energy zones common to all the atoms of the crystal lattice. Thus, due to this definite width of these zones, (and not sharp quantum levels of atoms) the probability of the absorbed energy of the ejected electron from the inner level lodging itself in a permitted zone being equal to that of the emitted energy due to the electron jump from the same permitted zone, may not be expected to hold good.

K Series :

Kievit and Lindsay [6] have shown experimentally that the K_{β_2} (K$\rightleftharpoons$N$_{II}$ N$_{III}$) line of Cu(29) coincides exactly with the principal K limit of Cu and have ascribed most of the K limits of elements from Cr(24) to Zn(30) to the transfer of electrons from the K levels to N$_{II}$ levels of the elements, the N$_{II}$ level being vacant for these elements. This is, therefore, a very strong support of the view that an emission line having a transition from a vacant level of an atom is due to the electron jump from the level which has already captured the electron ejected from an inner level by the absorption of energy.

The relation between the difference of ν/R values of K limits and K_{β_1} lines and the corresponding atomic numbers is shown in figure 7. Figure 8 shows the same thing for K_{β_2} for the corresponding elements.

In Table IV are given these values.

FIGURE 7.

$\frac{\Delta \nu}{R} \longrightarrow \quad [K - K_{\beta_2}] \longrightarrow$
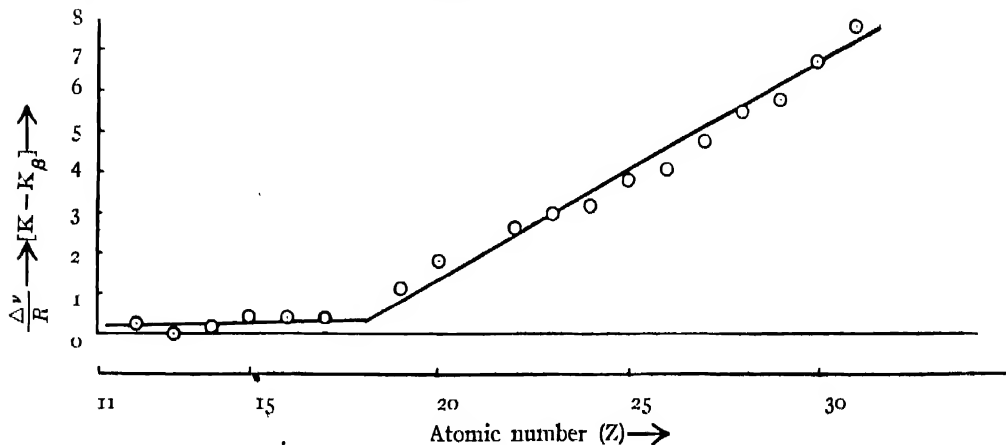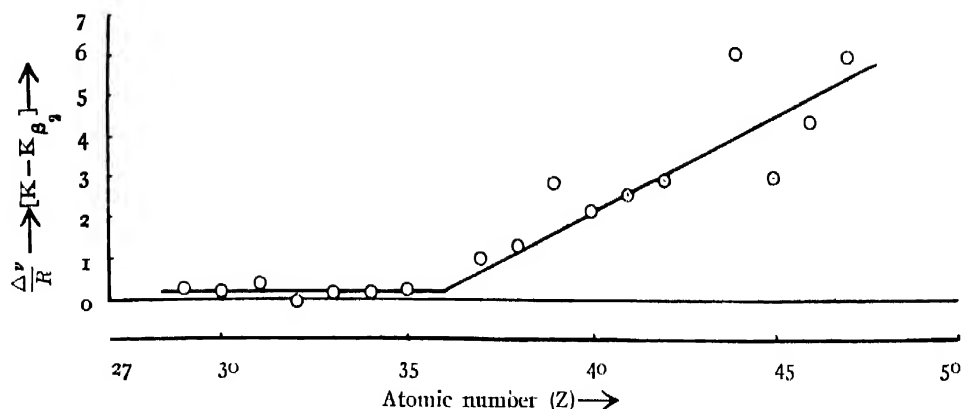
Atomic number (Z) $\longrightarrow$

FIGURE 8.

TABLE IV.

Atomic number (Z)	Number of electrons in M_{II} M_{III} level	ν/R for $K\beta_1[K \longleftrightarrow M_{III}]$	ν/R for K	Diff. between K and $K\beta_1$	Remarks.
12	...	95·57	95·8*	+0·23	*Taken from Sommerfeld's Atomic Structure and spectral lines [Third Edition, Revised, 1934].
13	1	114·76*	114·84	+0·08	
14	2	135·21*	135·38	+0·17	
15	3	157·41*	157·80	+0·39	
16	4	181·49	181·90	+0·41	
17	5	207·36	207·8	+0·44	
18	6				
19	6	264·38	265·60	+1·22	Diff. goes on increasing with (Z) as shown in Fig. 7.
20	6	295·54	297·38	+1·84	
21	6	328·52	331·17	+2·65	
22	6	363·20	365·80	+2·60	

Atomic number (Z)	Number of electrons in N_{II} N_{III} level	ν/R for $K\beta_2[K \longleftrightarrow N_{III}]$	ν/R for K	Diff. between K and $K\beta_2$	Remarks.
28	...	613·40	613·85*	+0·45	*Kievit and Lindsay's [6] value.
29	...	661·30	661·59	+0·29	
30	...	711·34	711·67	+0·33	
31	1	763·34	763·68*	+0·34	
32	2	817·58	817·57	−0·01	
33	3	873·86	874·01	+0·15	
34	4	931·85	932·0	+0·15	
35	5	992·39	992·57	+0·18	
36	6				Diff. goes on increasing as shown in Fig. 8.
37	6	1118·45	1119·4	+0·95	
38	6	1184·69	1186·0	+1·31	

The Kα lines Li(3), Be(4), etc., are also semi-opticals in the sense that the L$_{II}$ L$_{III}$ level is in a state of development from B(5) and there is no electron at all in L$_{II}$ L$_{III}$ level for Li and Be. The Kα lines for these elements are bands and have a width extending to several A.U. and consisting of, besides the main peak, many other maxima. The electron transition of these lines takes place from conduction levels, as suggested by O'Bryan and Skinner;[11] and therefore, the difference between the absorbed and the emitted quanta for the K level and the Kα lines for these elements becomes more significant which is evident from the complications arising from the width of the conduction levels.

M Series :

The agreement between the ν/R values of M$_{III}$ limit and the line (M$_{III}$←→O$_{IV}$) from the elements Lu(71) to Au(79) has also been shown by Sandstrom. The corresponding ν/R values of M$_V$ limit and Mα_1(M$_V$←→N$_{VII}$) lines from Ce(58) onwards are given below in Table V.

TABLE V.

Atomic number (Z)	Number of electrons in N$_{VI}$ N$_{VII}$	ν/R of Mα_1[M$_V$←——→N$_{VII}$]	ν/R of M$_V$	Diff. between M$_V$ and Mα_1	Remarks.
58	1	64·95	65·4	+ 0·45	
59	2		68·8		
60	3	72·04	72·5	+ 0·46	
61	4				
62	5	79·89	79·8	− 0·09	
63	6	83·36	83·8	+ 0·44	
64	7	87·67	87·7	+ 0·03	
65	8	91·89	91·7	− 0·19	
66	9	95·68	95·8	+ 0·12	
67	10	99·67	99·7	+ 0·03	
68	11	103·75	104·1	+ 0·35	
69	12				
70	13	112·20	112·9	+ 0·7	Diff. goes on
71	14	116·47	117·4 .	+ 0·93	increasing
72	14	121·12	122·7	+ 1·58	with (Z).
73	14	125·92	127·8	+ 1·88	

The values of ν/R for M$_V$ used in the above table V, are computed ones. That there is a discrepancy, due to combination defect, between the computed and the experimental values for M$_{III}$ and M$_V$ levels, has been stressed by Siegbahn.[12] But this discrepancy does arise in the case of M$_V$ and M$_{III}$ from W(74) to U(92).

CONCLUSION

Although it is only in some cases that the energy of the absorbed quantum has agreed almost exactly with that of a corresponding semi-optical line, the difference in the corresponding v/R values is never, of course, greater than 0.2 on the average in most of the cases. Also the discontinuity of all the particular curves shown, at the atomic number where the level in question is first completely filled up, gives justification in differentiating these so-called semi-optical lines from other X-ray lines. Lastly, it is to be mentioned that the photograph of some of these lines and some of the corresponding absorption limits (as has been done by Kievit and Lindsay [6] in cases of $K\beta_2$ of Cu and indirectly by Kawata [4] in the case of $L\beta_5$ of W and Pt on the same plate, will be more interesting and in a sense decisive. It will also throw more light on the process of absorption in these cases.

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HIGH-FREQUENCY MODULATION OF ULTRA-SHORT WAVES*

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INTRODUCTION.

Modulation of ultra-short waves has drawn the attention of various investigators in recent times owing to the growing application of these waves in transmission of pictures and television. In the case of transmission of speech or music the modulation is effected by low or audio frequencies only. But when the simultaneous transmissions of speech or music are required with television programmes, the problem of modulation becomes more complicated as the ultra-short carrier waves have to be modulated with high or video frequencies for the transmission of pictures along with the usual low-frequency modulation for speech. The method of amplitude modulation, which is generally used for the medium and short waves, is not so conveniently applicable in the case of modulation of ultra-short waves as the undesirable frequency modulation usually associated with amplitude modulation becomes more pronounced in the latter case. Further, when the modulation of ultra-short waves is accomplished by high frequencies, distortions, the slightest amount of which is detrimental for the pictures transmitted, may be caused by overloading of the modulation circuits due to the unavoidable capacities produced at high frequencies. The investigations of the methods of modulation of ultra-short waves by high frequencies from the above points of view have been found to be necessary. The present paper contains the results of study made by us, of the modulation of ultra-short waves of lengths 4 to 5 metres by frequencies of the order of 1·5 to 3 megacycles per second. A preliminary report of this has already appeared in Nature.[1] A pair of parallel wire high frequency transmission lines of suitable length has been used for effecting modulation in the present method. It has been shown mathematically that this method has the advantage of producing pure amplitude modulation entirely free from undesirable frequency modulation for transmission lines of lengths $\lambda/4$ and its integral multiples, λ being the wave-length of the carrier wave. This

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has been experimentally verified by the modified Lecher wire system as adopted previously by one of us.[2] This method of modulation has the further advantage that the capacity effects produced at high frequencies as mentioned above are also substantially minimised. It should be noted that Eastman and Scott[3] have applied the transmission lines of lengths $\lambda/8$ for producing frequency modulation of the carrier waves in the region of 300 metres by audio frequencies. The condition of frequency modulation derived by the above investigators has also been verified by us with ultra-short waves modulated by high frequencies. It is interesting to note that as the ultra-short waves are modulated by high frequencies, the side bands which are fairly separated from the carrier wave can be easily detected on the Lecher wire system. The actual frequencies of the side-bands produced are calculated and also verified experimentally by modulating the carrier wave by different high frequencies. In the case of frequency modulation sometimes more than two side-bands are exhibited.

THEORETICAL CONSIDERATIONS.

In the present method the amplitude modulation is produced by changing a part of the resistance of the oscillatory circuit of an ultra-short wave oscillator. If this resistance is made to form the sending or input end of a pair of transmission lines, it can be varied by changing the resistance of the receiving or output end of the same.

The following abbreviations will be used in the analysis below and in the subsequent sections :

f_o = frequency of the carrier wave.

f = frequency of the modulating wave.

l = length of the transmission lines.

n = any integral number.

R_o = surge impedance of the lines.

R_r = ohmic resistance at the receiving end.

R_s = ohmic resistance at the sending end.

X_s = reactance at the sending end.

Z_s = impedance at the sending end.

a = attenuation constant.

β = wave-length constant.

η = propagation constant per unit length.

θ = propagation factor (ηl).

If the receiving end impedance of the transmission lines be purely ohmic, the sending end impedance,

$$Z_s = R_o \left[\frac{R_r + R_o \tanh\theta}{R_o + R_r \tanh\theta} \right] \qquad \dots \text{(1)}$$

As the impedance at the sending end consists of the ohmic resistance R_s and the reactance X_s, it will be given by

$$Z_s = R_s + jX_s \qquad \dots \text{(2)}$$

and, since

$$\eta = a + j\beta$$

$$\therefore \quad \theta = (a + j\beta)l \qquad \dots \text{(3)}$$

Substituting the values of Z_s and θ in equation (1) and equating the real and imaginary parts separately, after neglecting the losses in the transmission lines, we get,

$$R_s = \frac{R_o^2 R_r}{R_o^2 \cos^2\beta l + R_r^2 \sin^2 \beta l} \qquad \dots \text{(4)}$$

and

$$X_s = (R_o^2 - R_r^2) \frac{R_o \sin \beta l \cos \beta l}{R_o^2 \cos^2 \beta l + R_r^2 \sin^2\beta l} \qquad \dots \text{(5)}$$

Further, by differentiating R_s and X_s with respect to R_r we get, from equation (4)

$$\frac{dR_s}{dR_r} = \frac{R_o^2 (R_o^2 \cos^2\beta l + R_r^2 \sin^2 \beta l) - 2R_o^2 R_r^2 \sin^2 \beta l}{(R_o^2 \cos^2\beta l + R_r^2 \sin^2 \beta l)^2} \qquad \dots \text{(6)}$$

and from equation (5),

$$\frac{dX_s}{dR_r} = - \frac{2R_o^3 R_r \sin \beta l \cos \beta l}{(R_o^2 \cos^2\beta l + R_r^2 \sin^2\beta l)^2} \qquad \dots \text{(7)}$$

In order that the amplitude modulation should be free from the undesirable frequency modulation, there must not be any change in the sending end reactance, when the receiving end resistance is varied. Hence, equating the left hand expression of equation (7) to zero, we get,

$$R_o^3 R_r \sin 2\beta l = 0$$

Since, R_o and R_r are not equal to zero,

$$\sin 2\beta l = 0,$$

$$\text{or, } \beta l = n\pi/2,$$

3

$\therefore l = \lambda/4$ or any integral multiple of this. Substituting this value of βl in equation (6), we get,

$$\frac{dR_s}{dR_r} = - \frac{R_o^2}{R_r^2} \qquad \qquad \dots \ (8)$$

and substituting the same in equations (4) and (5) we get,

$$R_s = R_o^2/R_r \qquad \qquad \dots \ (9)$$

and $\qquad\qquad X_s = 0 \qquad \qquad \dots \ (10)$

If the amplitude modulation is to be linear dR_s/dR_r must be constant. It will be observed, however, in equation (8) that R_o is a constant while R_r changes its value. Therefore dR_s/dR_r cannot remain constant. But the variation of the value of dR_s/dR_r will be minimum when $R_r = R_o$, and within a limited range of R_r the amplitude modulation will remain sufficiently linear.

EXPERIMENTAL ARRANGEMENT AND OBSERVATIONS

For the sake of convenience the experimental part is divided into two sections. In the first section, the condition of pure amplitude modulation is verified for a length of the transmission lines equal to $\lambda/4$ where λ is the wave-length of carrier wave. In the second section the modulated waves have been studied by means of modified Lecher wire system for different modulating frequencies. Short descriptions of these will be given below.

SECTION I.

As shown in figure 1, the transmission lines are connected at one end by a non-inductive high frequency resistance box (R_r) and the other ends are connected to two points across a suitable non-inductive resistance (R) which is a part of the oscillatory circuit of the ultra-short carrier wave generator. The current in
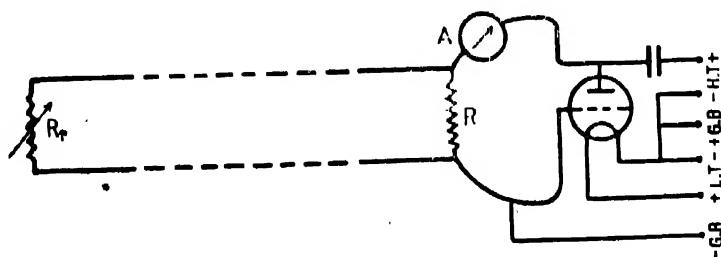
FIGURE I.

the oscillatory circuit could be measured with a thermomilliammeter (A). When the resistance R_r is varied the current in the oscillatory circuit changes, indicating thereby that the amplitude of the carrier waves is altered. That there is no change in the frequency of the carrier waves by the variation of R_r can be shown by measuring the wave-length of the carrier waves on a Lecher wire system. The values of R, given by equation (9) for different values of R_r have been verified experimentally for values of R_r nearly equal to R_0. All the values of R_r (Fig. 1) were measured directly, by noting the current passing through it with a thermo-milliammeter and measuring the potential difference between its two ends by a thermionic voltmeter. The values of resistance R, which acts in parallel with R not shown in the diagram, were measured by determining the actual resistance of R, the current through it and the total current through the oscillatory circuit.

Table I gives the values of the resistance R, for different values of resistance R_r in the vicinity of the surge impedance (R_0) of the transmission lines. Column I contains the actual values of R_r determined experimentally, and columns 2 and 3 contain respectively the observed and calculated values of the resistance R.

TABLE I.

Surge inpedance (R_0) of the transmission lines = 590 ohms.

R_r in Ohms.	R, in ohms (Ovserved).	R, in ohms (Calculated).
552	628	631
570	615	611
592	591	588
615	575	566
628	560	554

The experimental and the theoretical curves showing the variations of R, with R_r, when they are approximately linear, are plotted in figure 2. The continuous line represents the theoretical curve and the dotted one the experimental.
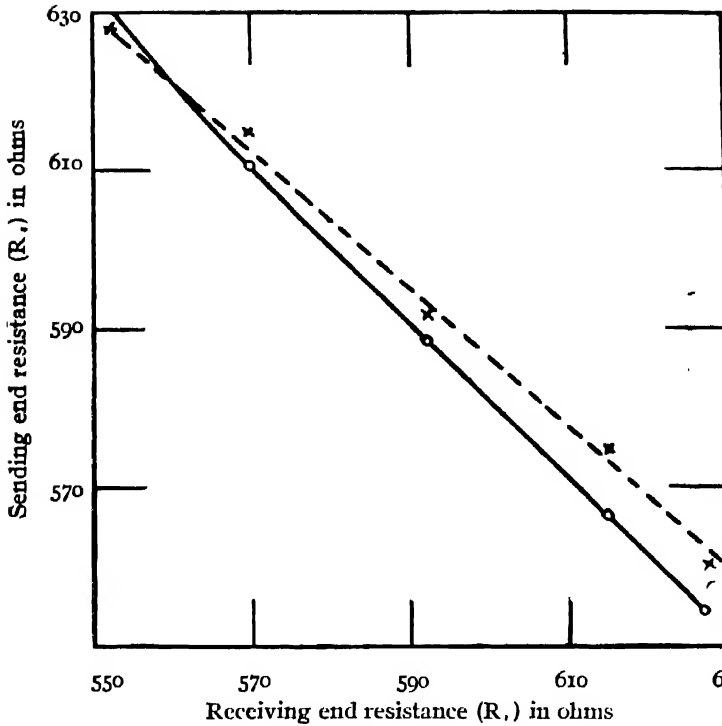
FIGURE 2.

SECTION 2.

The actual amplitude modulation of ultra-short waves with transmission lines was studied by an assembly of apparatus shown in figure 3. M represents the high frequency oscillator generating waves of the order of 100-200 metres for modulating the ultra-short waves generated by the oscillator (O). The valve (V), working over the linear portion of its plate current-grid voltage characteristic, acts as the receiving end resistance R_r. It should be mentioned that in order to obtain linear amplitude modulation, the impedance of the valve should be as
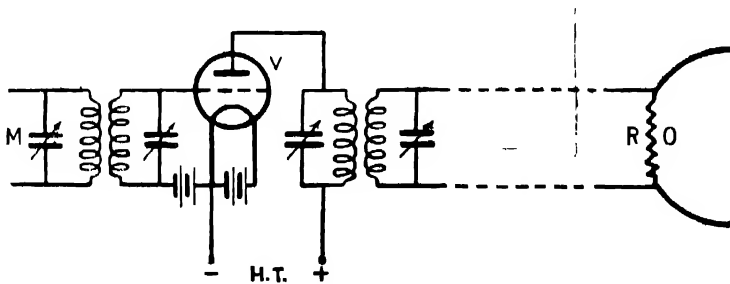
FIGURE 3.

far as possible equal to the surge impedance R_s of the transmission lines. The

tank inductance of the ultra-short wave oscillator is loosely coupled with the Lecher wire system. The side-bands are exhibited on the Lecher wires, when the ultra short carrier waves are modulated by different high frequencies.

The frequencies of the two side bands are measured and compared with those obtained theoretically for different modulating frequencies. It may be added here, that, pure frequency modulation can be produced by using transmission lines of length $\lambda/8$ and in this case, sometimes more than two side bands have been detected on the Lecher wire system.

Table II below gives the observed and calculated frequencies of the upper and lower side bands for different modulating frequencies.

TABLE II.

Carrier frequency (f_0) 61·22 megacycles/sec.

Modulating frequency (f) in megacycles per second.	Upper side band frequency in megacycles/sec ($f_o + f$)		Lower side band frequency in megacycles/sec ($f_o - f$)	
	Observed.	Calculated.	Observed.	Calculated.
1·50	62·70	62·72	59·76	59·72
1·67	62·94	62·89	59·59	59·55
2·00	63·19	63·22	59·16	59·22
2·31	63·55	63·53	58·88	58·91
3·00	64·18	64·22	58·25	58·22

SUMMARY AND CONCLUSION.

It has been shown theoretically that pure amplitude modulation of ultra short waves, free from undesirable frequency modulation can be produced by the use of a pair of parallel wire transmission lines of lengths $\lambda/4$, where λ represents the wave-length of the carrier waves. It has been further noted that linear amplitude modulation can only be produced if the resistance at the receiving end of the transmission lines is nearly equal to the surge impedance of the lines. The above results have been experimentally verified. With the proper choice of the wave-lengths of the modulating waves the upper and lower

side bands in the case of amplitude modulation are exhibited on a Lecher wire system. The frequencies of these side bands are verified for different modulating frequencies.

In conclusion we desire to express our sincere thanks to Principal P. Dutt, M.A. (Cantab.) for his valuable suggestions during the course of the investigations.

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LATTICE ENERGY OF KBr AND NaBr AND THE ELECTRON AFFINITY OF BROMINE.

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ABSTRACT. The lattice energies of KBr and NaBr have been experimentally determined from a study of the thermal ionisation of their vapours at temperatures between 1400°C—1650°C. and have been found to be 159K. cals and 176·3 K. cals respectively. By an application of the Born's Cycle the electron affinity of bromine has been calculated to be 80 K. cals. The results are in good agreement with theoretical calculations made from Born's theory, and other experimental data.

1. INTRODUCTION.

The present paper is an extension of the work done by Prof. M. N. Saha and the present author [1] on the "Experimental Determination of the Electron Affinity of Chlorine." Experimental determination of the lattice energies of alkali halides was made by J. E. Mayer [2] in 1930 who made a study of the thermal ionisation of the vapours of the iodides of caesium and potassium at temperatures of the order of 1150°K. He also calculated the electron affinity of iodine from his observations by an application of the Born Cycle. Mayer later on with L. Helmholtz [3] modified his apparatus for working at high temperatures and actually found out experimentally the lattice energies of RbBr and NaCl. They worked with a temperature as high as 1300°K, but even this temperature could not give them many observations with NaCl because it required even higher working temperatures. To meet out this difficulty a successful furnace was designed by Prof. Saha and the author [4] and experiments were made with KCl, NaCl and LiCl for determining the electron affinity of chlorine.[1] In the present paper the method has been extended to determine the lattice energies of KBr and NaBr and from it the value of the electron affinity of bromine has been calculated. Spectroscopic methods have also been used to determine the electron affinity and in this connection the work of Angerer and Müller[5] may be mentioned who observed the absorption spectrum

of the vapours of alkali bromides and attributed the beginning of the conti-
nuous absorption to absorption by Br^- and calculated the electron affinity.

The older theories for the lattice energy of ionic crystals gave only approxi-
mate results. In 1932, Max Born and J. E. Mayer [6] gave a successful theory
for the grating energies of ionic crystals which was in very good agreement
with the experimental data available at that time. They took into account the
null point oscillation energy, and the effect of Van der Waals cohesive forces
in addition to the Coulombian attractive force and a repulsive force between the
ions constituting the lattice. The repulsive force has been considered as an
exponential function instead of a power of the grating interval as was the case
in the old theory.

The lattice energy $\phi_{(r_0)}$ is the energy of the reaction

$$MX_{(solid)} = M^+_{(gas)} + X^-_{(gas)} - \phi_{(r_0)} \qquad \dots \ (1)$$
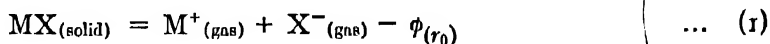
at absolute zero. MX represents an alkali halide. If L_{MX} be the heat of sub-
limation of the halide at $0°K$, the heat of dissociation of the gaseous halide
into an alkali and a chlorine ion according to the reaction

$$MX_{(gas)} = M^+_{(gas)} + X^-_{(gas)} - Q \qquad \dots \ (2)$$
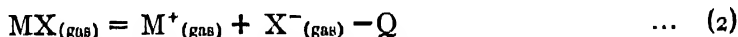
is given by

$$Q = \phi_{(r_0)} - L_{MX}. \qquad \dots \ (3)$$

From consideration of the Born Cycle the quantity Q is connected to the heat
of dissociation D of the halide, the ionisation potential of the alkali I_0. and the
electron affinity E_x of the halogen by the relation

$$Q = D + I_0 - E_x$$

Born and Mayer have given the following formula for the grating energy of
ionic crystals:—

$$\phi_{(r_0)} = - \frac{ae^2}{r_0} + \frac{C}{r^6} + (1-K)\frac{\rho}{r_0}\left\{\frac{ae^2}{r_0} + \frac{6c}{r_0^6} + \frac{3VT}{N}\left(\frac{\partial p}{\partial T}\right)_V\right\} + E \qquad \dots \ (4)$$

$$\text{where } K = \frac{(a-1)M'C_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{(\delta/\rho + 1 - a)r_0/\rho}}{2M + aM'C_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{(\delta/\rho + 1 - a)r_0/\rho}}.$$

$$C = S'_6 C + - + S''_6 \frac{C_{++} + C_{--}}{2}$$

$$E = \frac{9}{4} h\nu_{max}.$$

a = The Madelung number.

ρ = A constant for the alkali halides.

$$S_6' = \geqq \frac{1}{R^6} \text{ for the same kind of ions.}$$

$$S''_6 = \geqq \frac{1}{R^6} \text{ for different kind of ions.}$$

$\delta = r_- + r_+$ difference between the ionic radii.

M = Number of different kinds of neighbouring ions.

M' = Number of same kind of neighbouring ions.

$C_{++} = C_1$ = Interaction between two positive ions.

$C_{--} = C_2$ = Interaction between two negative ions.

C_{+-} = Interaction between two oppositely charged ions.

a = a constant quantity for a given crystal.

Helmoltz and Mayer[7] calculated the lattice energies of all the alkali halides according to the above equation and also found the electron affinity of the halogens. Recently their calculations have been revised by M. L. Huggins[8] who has used more recent data for r_+, r_-, compressibilities, Van der Waals attraction constants and other quantities entering into the equation. In table I, the calculated as well as the experimental values for the lattice energy of alkali bromides are given. The heats of sublimation of alkali bromides, the ionisation potential of the alkalies, the heats of dissociation of the alkali bromides and the theoretical as well as experimental magnitude of the electron affinity for bromine are also given in the table.

TABLE I.

Salt	L_{MX}	D	I_0	$\phi_{(r_0)}$ K. Cals.			E_x (K. Cals.)		
	K. Cals.	K. Cals.	K. Cals.	Helmholtz and Mayer.	Huggins.	Experimental.	Helmholtz and Mayer.	Huggins.	Experimental.
Li Br	43·4	102·3	123·8	188·3	189·5		81·2	80·0	
Na Br	51·6	86·0	117·9	174·6	175·5	176·3*	80·9	80·0	79·2*
K Br	50·4	90·6	99·5	159·3	161·3	159·7*	81·2	79·2	80·8*
Rb Br	49·0	90·5	96·0	153·5	156·1	151·3³	82·0	79·5	84·2⁹
Cs Br	46·9	91·9	89·5	146·3	149·6		82·0	78·7	

* Present paper.

The values for the electron affinity of the other halogens calculated accordin g to Born and Mayer's theory are

Halogen.	Helmholtz and Mayer (K. Cals.)	Huggins (K. Cals.).
Fluorine	95·5	93·4
Chlorine	86·5	85·1
Iodine	74·2	72·1

All the values mentioned above are in good agreement with experimental results. J. E. Mayer [2] found that the electron affinity of iodine is 72·6 ± 2 K. cals. and later on P. P. Sutton and J. E. Mayer [9] obtained a value of 72·4 ± 1·5 K. cals. from another different method. From their experiments on NaCl L. Helmholtz and J. E. Mayer [3] obtained a value of 88·3 K. cals. for the electron affinity of chlorine. M. N. Saha and the present author [1] worked with KCl, NaCl and LiCl and obtained a value of 86·6 K. Cals. In the present investigation on bromine the value obtained is 80 K. Cals. which is in good agreement with the values given in table 1, and also with the value 84·2 K. Cals found by L Helmholtz and J. E. Mayer [3] from their experiments on RbBr.

2. THEORY.

If MBr denotes an alkali bromide molecule, the dissociation process at any temperature can be represented by the following set of equations:—

$$MBr \rightleftharpoons M + Br - D. \qquad \qquad \dots \quad (5)$$

$$MBr \rightleftharpoons M^+ + Br^- - Q. \qquad \qquad \dots \quad (6)$$

$$M \rightleftharpoons M^+ + e - I_0. \qquad \qquad \dots \quad (7)$$

$$Br^- \rightleftharpoons Br + e - E. \qquad \qquad \dots \quad (8)$$

$$Br_2 \rightleftharpoons 2Br - D'. \qquad \qquad \dots \quad (9)$$
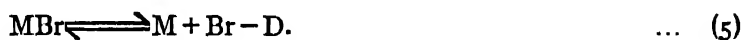
D' is the heat of dissociation of bromine. The dissociation of diatomic molecules has been theoretically worked out by Gibson and Heitler [10] who have taken into account the translational, rotational, vibrational states of the molecules and also the effect of nuclear spin. If K_1, K_2, K_3, K_4, and K_5 be the equilibrium constants of the reactions represented by the equations (5) to (9) then we have

$$\log K_1 = \log \frac{p_\text{M} p_\text{Br}}{p_\text{MBr}} = -\frac{D}{2\cdot3RT} + \frac{3}{2}\log T + \log\left(1 - e^{-\frac{h\nu}{kT}}\right)$$
$$+ \log\left[\frac{2^{\frac{3}{2}} K^{\frac{3}{2}}}{\pi^{\frac{1}{2}} Ih}\left(\frac{m_\text{MBr}}{m_\text{M} m_\text{Br}}\right)^{\frac{3}{2}}\right] \quad \dots \text{(10)}$$

$$\log K_2 = \log \frac{p_\text{M}^+ p_\text{Br}^-}{p_\text{MBr}} = -\frac{Q}{2\cdot3RT} + \frac{3}{2}\log T + \log\left(1 - e^{-\frac{h\nu}{kT}}\right)$$
$$+ \log\left[\frac{K^{\frac{3}{2}}}{2^{\frac{3}{2}}\pi^{\frac{1}{2}} Ih}\left(\frac{m_\text{MBr}}{m_\text{M} m_\text{Br}}\right)^{\frac{3}{2}}\right] \quad \dots \text{(11)}$$

$$\log K_3 = \log \frac{p_\text{M}^+ p_e}{p_\text{M}} = -\frac{I_0}{2\cdot3RT} + \frac{5}{2}\log T + \log\frac{(2\pi m_e)^{\frac{3}{2}} K^{\frac{5}{2}}}{h^3} \quad \dots \text{(12)}$$

$$\log K_4 = \log \frac{p_\text{Br} p_e}{p_\text{Br}^-} = -\frac{E_x}{2\cdot3RT} + \frac{5}{2}\log T + \log\frac{(2\pi m_e)^{\frac{3}{2}} K^{\frac{5}{2}}}{h^3} \quad \dots \text{(13)}$$

$$\log K_5 = \log \frac{p_\text{Br}^2}{p_\text{Br}_2} = -\frac{D^1}{2\cdot3RT} + \frac{3}{2}\log T + \log\left(1 - e^{-\frac{h\nu}{kT}}\right)$$
$$+ \log\left[\frac{m^{\frac{3}{2}} K^{\frac{3}{2}}}{4\pi^{\frac{1}{2}} Ih}\right] + \log 8. \quad \dots \text{(14)}$$

I is the moment of inertia of the molecule. The dissociation constants K_1, K_2, K_3, and K_4 are connected by the relation

$$K_2 = \frac{K_1 K_3}{K_4}$$

Also from consideration of Born's cycle we get $E = D + I_0 - Q$ $\qquad \dots \text{(15)}$

and $\qquad\qquad\qquad \phi_{(r_0)} = Q + L_\text{MX}$ $\qquad \dots \text{(16)}$

The magnitude of the dissociation constant K_2 is determined experimentally at different temperatures and from it the value of Q is calculated. As the heats of dissociation and sublimation of the alkali halides and the ionisation potentials of the alkalies are well known the electron affinity of bromine and the lattice energy is easily calculated with the help of equations. (11), (15) and (16)

3. EXPERIMENTAL.

The present work deals with an experimental study of the thermal ionisation of the bromides of sodium and potassium at high temperatures. The salt was heated in an electric furnace and the vapour was allowed to enter a region of high temperature where it suffered dissociation into atoms as well as ions according to the equations (5), (6), (7), (8) and (9). The demountable vacuum graphite furnace

described in a previous paper by M. N. Saha and A. N. Tandon [4] was used for the production of high temperature. The experimental procedure and the internal arrangements inside the furnace have also been described elsewhere.[1] The temperature of the graphite tube was recorded by means of a disappearing filament type of pyrometer capabale of reading temperature accurately within 10°C, the temperature at which the salt vaporised was measured by a nickel-nichrome thermocouple. From the temperature of the furnace the vapour pressure could be easily calculated.

The products of dissociation from the graphite tube escaped through a narrow circular opening, then passed through a limiting diaphragm, and were finally collected by a Faraday cylinder connected to a galvanometer. By giving the Faraday cylinder a small positive or negative potential with respect to the graphite tube (which is always kept at earth potential) the current due to the negative bromine or the positive alkali ions could be easily measured. The partial pressure of the ions could be easily calculated from the magnitudes of the ion currents.

If i_g denotes the current recorded by the galvanometer, the magnitude of the total effusion current $i_M{}'$ (due to the positive ions) is given by

$$i_{M^+} = \frac{2d^2}{r2}\, i_g$$

where d is the distance between the effusion hole and the limiting diaphragm, and r the radius of the diaphragm. The effusion current is related to the partial pressure $p_M{}^+$ inside the tube by the relation

$$i_{M^+} = \frac{S}{4}\, \frac{p_M{}^+}{k'T}\, e\, \sqrt{\frac{8kT}{m\pi}}$$

where S is the area of the effusion hole, T the absolute temperature of the graphite tube, m the mass of ion in absolute units, k the Boltzman constant and e the electronic charge. We have therefore

$$p_{M^+} = \frac{i_{M^+}}{eS}\, \sqrt{2\pi m_M k'T}$$

Similarly,

$$p_{Br^-} = \frac{i_{Br^-}}{eS}\, \sqrt{2\pi m_{Br} kT}$$

The experimental value of the dissociation constant K_2 is therefore given by

$$K_2 = \frac{p_{M^+} p_{Br^-}}{p_{MBr}} = \frac{i_{M^+} i_{Br}}{e^2 S^2}(2\pi kT)\frac{\sqrt{m_M m_{Br}}}{p_{MBr}} \qquad \ldots \ (17)$$

4. RESULTS.

The results obtained for sodium and potassium bromides are given in tables 2, and 3 respectively. In the second column of the tables the vapour pressure of salt at which that observation was taken is given. The vapour pressure of KBr has been calculated from the empirical formula of Fiöch and Rodebush [11]

$$\log p_{mm} = -\frac{8780}{T} + 8 \cdot 2470$$

For NaBr the older formula of von Wartenburg and Albrecht [12] has been used

$$\log p_{atm.} = -\frac{38580}{4 \cdot 57T} + 5 \cdot 0675$$

In the fourth and fifth columns of the tables the magnitude of the positive and negative ion current is given for the diameter of the effusion hole given in the first column. The last three columns contain the values of the equilibrium constant, Q and the lattice energies respectively. The mean values for the lattice energy of KBr and NaBr come out to be 159·7 K. Cals and 176·3 K. Cals respectively. The electron affinity for bromine as calculated with KBr comes out to be 80·8 K. Cals while with NaBr it is 79·2 K. Cals. These experiments therefore give a mean value of 80 K. Cals. for the electron affinity of bromine.

TABLE II

Diameter of the effusion hole (mms.)	Vapour pressure (dynes/cm.²)	Temperature of the graphite tube (°C)	$i_k{}^+ \times 10^5$ (amps.)	$i_{br}{}^- \times 10^5$ (amps·)	$K_2 \times 10^4$	Q K. cals.	$\phi_{(r_0)}$
1·05	44·53	1620	8·853	7·568	93·33	107·4	157·8
,,	78·11	1610	9·044	7·752	55·43	108·7	159·1
,,	28·96	1590	5·714	3·809	45·84	108·2	158·6
,,	12·73	1570	2·879	2·252	30·74	107·6	158·0
,,	19·13	1550	3·273	2·067	17·62	109·2	159·6
,,	85·53	1550	5·078	3·174	11·28	111·3	161·7
,,	38·96	1520	4·121	2·905	18·03	107·3	157·7
,,	20·97	1470	1·668	1·315	5·967	108	158·4
,,	17·85	1460	1·374	1·001	4·369	108·4	158·8
,,	26·89	1435	0·849	0·738	1·303	110·9	161·3
1·17	227·9	1570	11·03	9·99	24·08	109·4	159·8
,,	69·45	1555	4·988	4·357	15·48	110·1	160·5
,,	31·46	1550	3·538	2·692	14·90	109·7	160·1
,,	22·48	1550	2·819	2·435	14·97	109·7	160·1
,,	227·9	1525	9·221	7·60	15·13	108·2	158·6
,,	75·63	1520	3·717	2·819	6·713	110·9	161.3
,,	54·17	1490	2·845	2·308	5·771	107·4	159·8
,,	31·46	1480	1·718	1·358	3·521	110.5	160·9
,,	75·63	1400	1·23	0·948	0·697	119·9	161·3

Average of Lattice energy = 159·7 K. Cals.

A. N. Tandon

TABLE III.

Diameter of the effusion hole (mms.)	Vapour pressure (dynes/cm²)	Temperature of the graphite tube (°C)	$i_{Na^+} \times 10^6$ (amps.)	$i_{Br^-} \times 10^6$ (amps.)	$K_2 \times 10^6$	$\overset{Q}{K. \ Cals.}$	$\phi_{(r_0)}$
1·17	31·7	1620	9.228	5·895	67·41	126	177·6
,,	14·89	1600	4·86	3·076	39·08	126·7	178·3
,,	66·99	1560	10·13	5·725	33·69	124·4	176·0
,,	52·84	1500	4·184	2·642	7·695	125·3	176·9
,,	66·99	1475	5·064	2·863	7·845	123·4	175·0
,,	52·84	1410	1·64	0·991	1·081	125·2	176·8
,,	94·19	1400	2·312	1·212	1·031	124·7	176·3
1·58	38·64	1640	25·09	17·33	134·4	124·7	176·3
,,	123·1	1600	28·68	21·51	58·49	125·1	176·7
,,	52·84	1555	12·55	8·366	22·67	125.4	177·0
,,	43·55	1540	10·16	7·171	18·92	125	176·6
,,	38·64	1525	9·561	5·975	16·44	122·5	174·1
,,	123·1	1500	11·95	8·067	8·672	124·8	176·4
,,	52·84	1470	5·378	3·885	4·299	125·1	176·7
,,	43·55	1460	5·974	4·183	6·204	123	174·6

Average of Lattice energy = 176·3 K. Cals.

5. DISCUSSION OF RESULTS.

It can be easily seen that the experimental lattice energies for K Br and NaBr are in good agreement with the theoretical values given in table 1. The electron affinity of bromine which has been found to be 80 K. Cals is also in fairly good agreement with the theoretical values and also with the experimental value of L. Helmholtz and J. E. Mayer[3] (84·2 K. Cals). According to theory, the positive and negative ion currents should be inversely proportional to their atomic weights. This relation is satisfied in both the cases within an accuracy of 15%, but a noticeable feature is that in most of the observations this ratio is less than the theoretical value which should be 1·432 for KBr and 1·865 for NaBr. This can only be attributed to the presence of free electrons inside the graphite tube, the effect of which will be to increase the number of negative bromine ions according to equation (8) and to diminish the number of alkali ions according to the equation (7). Evidently these free electrons are the thermally liberated electrons from the graphite tube at that temperature. The current due to these electrons was found to be negligible in comparison to the ion currents. (This was found by performing experiment without any salt in the subsidiary furnace.)

The deviation from the theoretical ratio has also been noticed by Helmholtz and Mayer[3] in their investigations on RbBr and NaCl, but they found that the positive ion current was larger than its theoretical value. For sodium chloride they have taken very few measurements and so nothing decisive can be told. They attribute the abnormal value of the ratio to the formation of an ion sheath round the effusion hole on account of the existence of a contact potential between

the gas inside the oven and the surface surrounding it. The formation of such a sheath will accelerate one kind of ions and retard the other. This explanation appears to be correct but does not seem to account for the increase of one particular kind of ion current.

In the investigation of the electron affinity of chlorine by M. N. Saha and the author it was observed that the positive ion current was much larger than the negative ion current in the case of sodium chloride. It was argued that this diminution of the negative current was due to the formation of molecular chlorine. This interpretation was based on a wrong calculation and cannot be taken as correct. At the temperatures and pressures used in the experiment more than 99% of the chlorine would exist in the atomic state. This can be tested with the help of equation (14). It was thought that in Helmoltz and Mayer's experiment the abnormally large positive ion current was due to this cause on account of working at low temperatures (1300° K), but even at this temperature only 4% of bromine will exist in the molecular state, at the pressures used in the experiment.

The limits of experimental error in such experiments have been thoroughly discussed by J. E. Mayer[2] and later on by Helmholtz and Mayer[3] who showed that the probable error is not more than ±2·5 K. Cals.

I wish to express my sincere thanks to Prof. M. N. Saha, D.Sc., F.R.S., for his invaluable guidance and help throughout this work. Our thanks are also due to the Royal Society of London for giving a grant of £150 which enabled us to construct the furnace and buy its accessories.

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METEORS AND UPPER ATMOSPHERIC IONIZATION.

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ABSTRACT. The present work is an extension of the investigations on the effect of meteoric shower on the E region of the ionosphere which were begun at Calcutta in 1933. In the previous work, on account of insufficient frequency range, the effect of meteors on the F regions could not be studied. This has now been rectified and the present investigation has been made possible.

Results of observations showed that the ionization of the E_1 and E_2 regions increased enormously above its normal value during the Leonid meteoric shower of 1936—in the early hours of the mornings of November 15 and 16.

No appreciable change in the ionization of the F_1 and F_2 regions occurred in these hours. There was an increase of F_1 ionization at about midnight on November 15, but this may be ascribed to a magnetic storm which was in progress during that night.

The absence of any increase of ionization of the F_1 and F_2 regions due to meteoric impact is explained after the Lindemann-Dobson theory of meteors.

§ 1. INTRODUCTION.

It has been known from some time past that meteoric showers affect radio reception. Pickard in 1921 was the first to notice the effect. In 1930 Skellet, considering the available data came to the conclusion that the total amount of energy received by the earth from meteoric impact could be as much as 1/14th[1] of that of sunlight and is mainly expended in ionizing the medium through which the meteors pass. Since then a number of direct observations on the ionization of the upper atmosphere in relation to the incidence of meteoric showers have been made in the United States,[2] India[3] and Japan.[4] All these observations, which were made on the lower E region of the ionosphere situated at a height of about 100 km., showed definitely that the ion-content of this region increases enormously during a meteoric shower. The meteors are, however, known to shine in considerable numbers at levels much higher than that of the E region. It was therefore thought that fruitful results would be obtained if fresh observations on the effect of meteors were made with particular attention to the higher regions of the ionosphere above the normal E region, *viz.*, the E_2, F_1 and F_2 regions.

Investigation with this object in view was carried out during the Leonid shower of 1936 and the results obtained are described in this paper.

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§ 2. METEORIC SHOWERS.

It may perhaps be useful here to describe the main features of the Leonid and of the other similar showers which occur at regular intervals. The meteors are particles of masses ranging from a few milligrams to several hundreds of kilograms, which move in swarms round the sun in fixed orbits of definite shape and size. The orbits are not infrequently those of defunct or disintegrated comets. The meteoric particles, as they are called, are scattered throughout these orbits so that whenever the earth crosses one of them, the meteors are attracted into its atmosphere. As they rush through the atmosphere they collide with the air molecules with the result that the heat developed vaporises the particles and makes them glow and appear as meteoric shower.

The particles moving in a particular orbit constitute what is known as a meteoric family. We give below a list of the better known meteoric families with duration of the corresponding showers and the dates on which the strength of each shower is maximum.

TABLE I.

Name.	Duration.	Date of Annual Maximum.
Perseids	35 days	August 11-12
Orionids	14 ,,	October 19-23
Leonids	3 ,,	November 14
Andromedids	2 ,,	November 24
Geminids	14 ,,	December 11-13

It should be noted that the distribution of the meteoric particles in a particular orbit is not uniform throughout the orbit. There is a main shoal of particles outside which they are relatively sparsely distributed. If the earth, in its annual round, crosses the track of a certain family when the main shoal happens to be nearest to the ecliptic, then this particular family provides maximum display of shooting stars. In case of the Leonids, this maximum occurs at intervals of about 33 years.

The names of the different families as seen in the above table are generally associated with certain constellations. This is because of the fact that if the observed paths of the meteors belonging to a particular group be projected on the celestial globe it is seen that all these paths meet approximately at a certain point. The name of the shower corresponding to this group is derived from the constel-

lation in the celestial sphere in which this point, called the radiant, is situated. For example, we call the Leonids as such because its radiant is in the constellation Leo.

Besides the groups of meteors associated with definite radiants, the earth also encounters sporadic meteors which are known to emanate from interstellar space and have no fixed radiants. The shower meteors are all particles connected with our solar system whereas the sporadic ones are of extra-solar origin.

In recent years great improvements have been made, notably in the United States, in the methods of observing meteoric phenomena. Results of such observations show that the velocity of the meteors vary within wide limits. Telescopic observations reveal that the highest velocity attained may be up to 200 km./sec. while the velocity of those observed with the naked eye may be as low as 10 km./sec. The heights of appearance and disappearance also lie within a wide range. The highest altitude at which meteors have been observed appear to be within the F regions of the ionosphere. There is no lower limit of the height of disappearance since the falling of glowing meteors on the ground is not an uncommon phenomenon.

A general relation seems to exist between the heights of appearance and disappearance with the velocity of a meteor. A meteor having greater velocity appears higher up and also disappears higher in the atmosphere than one moving with a lower velocity.

The composition of meteors varies considerably from type to type, the chief constituents being iron, calcium, magnesium, etc. Generally speaking, meteors belonging to our solar system, *i.e.*, the shower meteors are mostly composed of rocky materials such as are found in terrestrial rocks. The sporadic ones, which are of extra-solar origin are mainly of pure iron.

§ 3. THEORETICAL CONSIDERATIONS.

Let us consider the processes by which it may be possible for the meteors to produce ionization or to increase the same if it were already in existence. For this purpose we will have to call to our aid the various theories which have been proposed from time to time to explain the meteoric phenomena.

Let us assume, as is most probable, that the atmosphere at or above 100 km. from the surface of the earth consists mainly of nitrogen and oxygen. If an atom of nitrogen (or oxygen) is struck by a meteor moving with a velocity of 40 km./sec., then, if the collision is supposed to be inelastic, the total energy imparted to the molecule is approximately that corresponding to 230 (or 262) electron volts.

The nature of the immediate effect of the impact of air molecules on the surface of the meteor has been discussed by various authors. Sparrow[5] assumes

that the heat imparted to the meteor due to the impact is sufficient to vaporise it and produce a cap or mantle of vapour in front of it. Lindemann and Dobson,[6] who have studied meteoric phenomena in great detail, are, however, of opinion that the first impact does not impart sufficient heat to cause appreciable vaporisation of the meteoric material but that the rush of the meteor compresses adiabatically the air in the neighbourhood of its front surface and as a result an air cap is formed. Subsequent impacts of air molecules on this air cap raises its temperature to a sufficient degree to impart part of its heat to the meteor and cause vaporisation.

We may now consider which of these two possible processes favours ionization. In the first case collision occurs between air molecules and the molecules of the vapour of the meteoric material and in the second case the collision is between air molecules of the atmosphere and those of the gas cap. Now, recent investigations on ionization by collision between neutral molecules show that it is much easier to produce ionization when the colliding molecules are of the same kind than when they are of different kinds.[7] In fact it has not yet been possible to detect ionization by collision between neutral molecules of different kinds though it has been possible to produce the same for similar molecules (e.g., of Ne, A or other rare gases) with energies of about 30 to 60 electron-volts.

It thus seems that according to the Lindemann-Dobson process in which the colliding molecules are of the same kind, the possibility of production of ionization in the upper atmosphere by the impact of meteors is much greater.

Results of our observations to be described later also provide an independent evidence of the correctness of the essential features of the Lindemann-Dobson theory. According to this theory the density of the atmosphere at which the cap of air begins to be formed in front of a meteor is related to the velocity and radius of the meteor by the relation

$$\rho = 5\cdot6 \times 10^{-4}/rv$$

where r is the radius in cms.

and v is the velocity in cm./sec.

Taking the most common velocity as 40 km./sec. and the average radius as 1 mm., the density at which the cap begins to form is found to be $1\cdot4 \times 10^{-9}$ gm./cc.

It is possible to calculate the height at which this density will occur. If isothermal distribution at a temperature of $220°$K is assumed to exist throughout the whole of the atmosphere above the level of the tropopause so that

$$\rho = \rho_0 e^{-Mgh/RT}.$$

this density is found to be attained at a height of about 90 km. Lindemann and Dobson have, however, obtained quite a different distribution of atmospheric density from meteoric data. For convenience we give below two curves, one (broken) depicting the variation of density with height as given by these authors, and the other (continuous) as obtained on the assumption of an isothermal atmosphere at 220°K. The thick full line portion is obtained from " sounding balloon " observations. It will be seen that the density falls much less rapidly in the former case and the value of $\rho = 1 \cdot 4 \times 10^{-9}$ gm./c.c. is attained at a height of about 200 km.* Now, in our observations, as will be described later, we have found that only the ionospheric layers which lie below this height
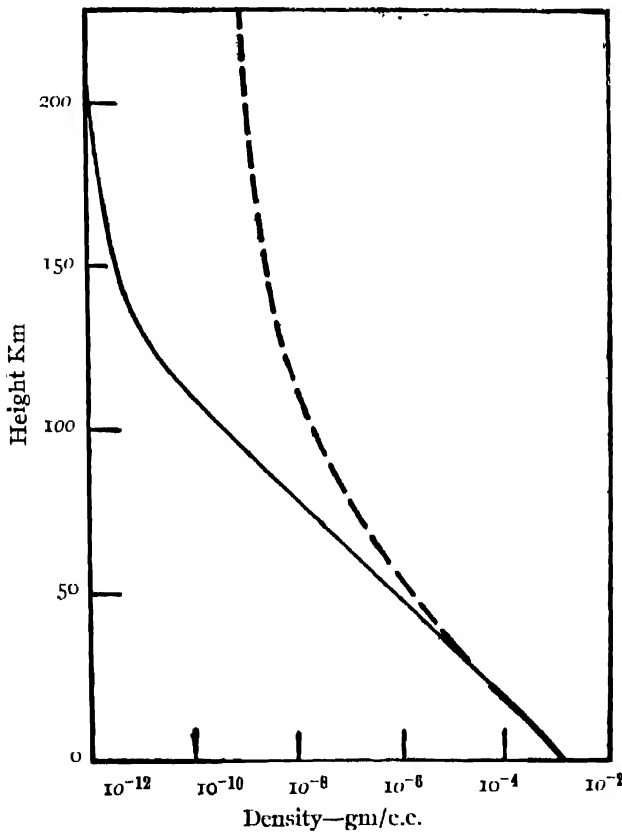
FIGURE 1.

experience increase of ionization due to a meteoric shower. The upper F_1 and F_2 layers are not affected in any way. The absence of any change of ionization in

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* It may be noted here that from their theory of meteors Lindemann and Dobson arrive at the conclusion that the temperature of the atmosphere begins to increase considerably from a height of about 60 km. instead of remaining constant, as hitherto assumed. Recent observations on the anomalous propagation of sound waves definitely indicate that such a temperature inversion exists, although the level of inversion is estimated at a somewhat lower height. (See Handbuch der Geophysik by Dr. B. Gutenberg, Vol. 9, Part I; (1932).)

these higher regions receives an easy explanation on the Lindemann-Dobson hypothesis. If the density distribution of Lindemann and Dobson really exists then the atmospheric density above 200 km. is such that it does not favour cap formation in front of an average meteor. The impact of the meteors will therefore have no effect on the regions above this level.

In this connexion another interesting point has to be considered. We have assumed till now that the meteor is rushing through unionized air, that is, the air molecules which form the gas cap or which collide with it are all neutral. Really, however, the meteor, in passing through the various regions of the ionosphere, meets with atmospheric layers which are ionized to different degrees. The question arises—how far ionization already existing will promote further ionization. We thus have to consider the effect of collision of electrons and of positive and negative ions of nitrogen and oxygen with the air molecules forming the gas cap. The effect of electrons is negligible since the energy of an electron with a velocity of 40 km./sec. corresponds to only about $4 \cdot 5 \times 10^{-3}$ electron-volts. For the case of the ions, however, the energy is much higher and corresponds to about 230 and 262 electron-volts respectively. Experimental data on the probability of ionizing air molecules by oxygen and nitrogen ions of this energy are not available. We may, however, draw some conclusions from data which are available for heavy positive ions of potassium, rubidium, etc. It has been found that[8] alkali ions of energy equivalent to only 150 electron-volts produce detectable ionization by collision with rare gas molecules. For the case of negative ions data are lacking but it is probable that ionization with negative ions is easier than with positive ions since the escaping electron in the former case will, at the moment of ejection, find itself in a more or less neutral field due to the combined effect of the impinging negative ion and the positive ion which is produced. It is not unreasonable to assume that oxygen and nitrogen ions (positive or negative) having energies of not a very different order of magnitude will also be able to ionize air molecules. It is therefore possible that the ionization which already exists in the different layers of the ionosphere will be a contributory cause to the very large increases which have been observed. For levels above 200 km., however, since the air cap is not likely to be formed at all, the question of ionization by impact of nitrogen and oxygen ions if they already exist—as in the F_1 or F_2 layers—does not arise.

§ 4. EXPERIMENTAL RESULTS.

The experimental arrangement employed in our observations was based on the well-known group-retardation method of Breit and Tuve. The critical penetration frequency method was made use of in measuring the ionization density of the ionospheric regions. The range of frequency employed extended from 1 mc./sec. to 15 mc/sec. The transmitter and receiver were located in the same room.

Since the Leonid meteoric shower occurs with maximum intensity on the 14th of November every year as stated above and lasts for about three days it was decided to keep hourly records of the ionic densities of the different ionized regions for five consecutive nights commencing from the night of November 12-13. The observations were made every hour from 2200 hours till 0530 hours in the morning. Each observation which comprised the measurement of ionization of all the layers that might exist at the time lasted from 10 to 15 minutes. No observations were made at 2300 hours.

Since the ionic density is given by

$$N = 1.28 \times 10^{-8} f^2$$

where N is the number of electrons per cm.^{3}

and f is the critical penetration frequency in cycles per sec.,
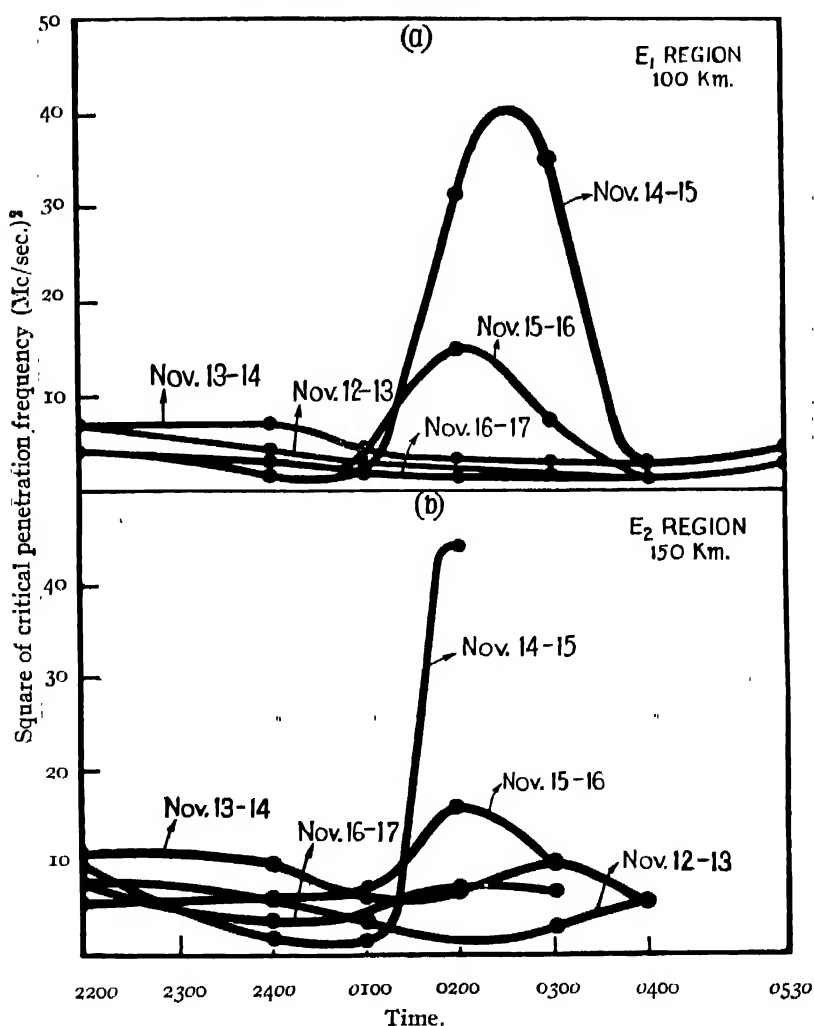
FIGURE 2.

we have plotted the value of f^2 against time for each night of observation and for each of the ionized regions E_1, E_2, F_1 and F_2. The average heights of these regions were 100, 150, 210 and 270 kms. respectively. It will be noticed in the curves given below (Figs. 2 and 3) that the E_2 and F_1 echoes could not be observed at all hours of the night especially during the latter part, as the absence of dots representing the ionization indicates.
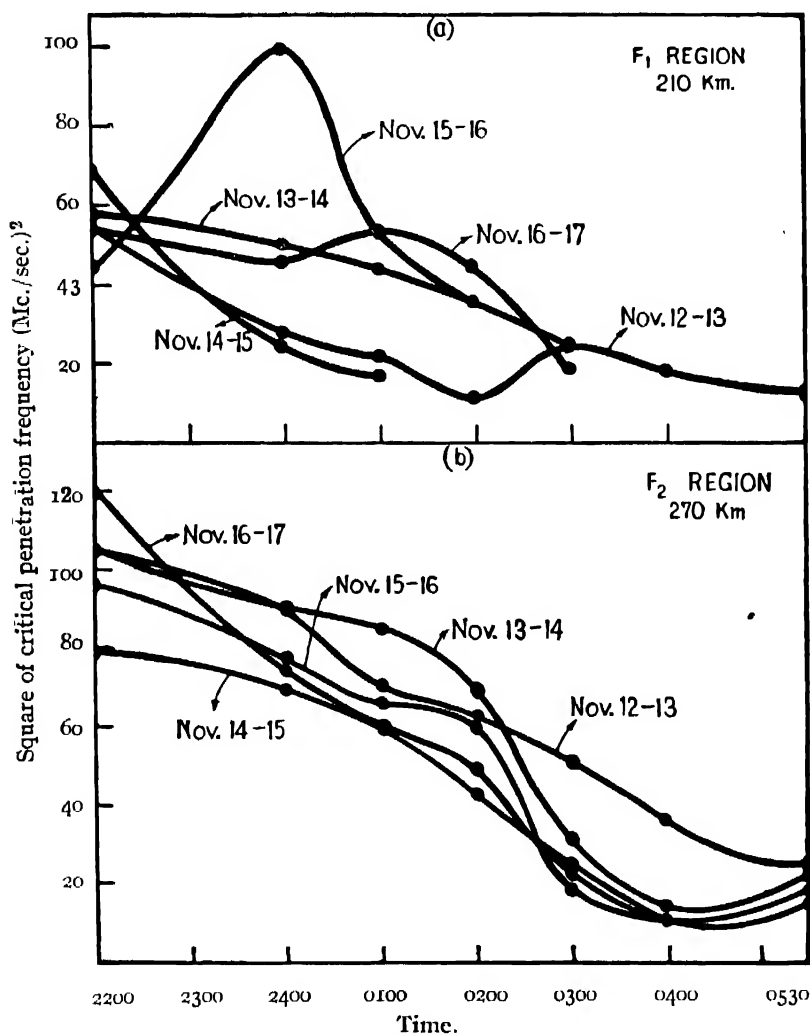
FIGURE 3.

It will be seen in figure 2 (a) that the ionization of the E_1 region has gradually diminished till the early hours of the morning in the nights of November 12-13, 13-14 and 16-17. But on the night of November 14-15 the ionization, instead of following the normal course of gradual diminution has undergone an abnormally high increase at about 0200 hours and then has fallen to the normal value at about 0400 hours. Almost the same phenomenon occurred on the night

of November 15-16 but the increase of ionization had been less marked than on the previous night.

In figure 2 (b) the hourly variation of ionization of the E_2 region has been depicted. It is seen that the ionic density of this region followed the same course as that of the E_1 region on all the nights. Only the drop of ionization after the maximum on the night of November 14-15 could not be observed presumably because the ionization fell below that of the E_1 region.

In figures 3 (a) and (b) it will be seen that the ionization of the F_1 and F_2 regions, apart from minor irregularities, gradually diminished as night advanced and fell to a minimum nearabout sunrise on all the nights. But a remarkable exception occurred on the night of November 15-16 in the case of the F_1 region. It will be noticed that on this night the ionization of this region suffered an abnormal increase at about midnight.

The increases in the ionization of the E_1 and E_2 regions on the night of November 14-15 are undoubtedly due to the impact of meteors. There was no other disturbing factor in this night which might account for these abnormalities. There might be some uncertainty with regard to the increases on the night of November 15-16 in E_1, E_2 and F_1 ionization, as there was a magnetic storm in progress during that night. Since, however, the time of increase in the ionizations of E_1 and E_2 on this night, corresponds, as on the previous night, to the hour of maximum intensity of the Leonid shower and also since no significant correlation between a magnetic storm and abnormal increase of the ionizations of these regions has, as yet, been found in our latitude it may safely be inferred that these increases were also due to the meteoric shower. With regard to the increase in the F_1 ionization on the same night it is very doubtful if meteors were responsible for this since the time of increase does not correspond to the time of maximum shower. Further, as in the case of the two E regions, there was no increase of a similar nature on the previous night.

§ 5. CONCLUSION.

The experimental observations prove conclusively that the lower E_1 and E_2 regions of the ionosphere are strongly affected by the meteoric shower while the higher F_1 and F_2 regions are not so affected. The explanation of this phenomenon is obtained from the hypothesis of gas cap formation suggested by Lindemann and Dobson. As mentioned before if we accept the density distribution obtained by Lindemann and Dobson from meteoric data, we find that the atmosphere at heights above 200 km. is not dense enough to favour gas cap formation in front of an average meteor. The meteors therefore pass through the F_1 and F_2 regions which are situated above this level without affecting their ionization in any way.

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It might appear at first sight that the impact of the meteors would produce more or less uniform ionization in the whole mass of air between 160 and 60 km., the region of the most frequent appearance and disappearance of meteors. If, however, we remember, as has been explained above, that a region which is already ionized should undergo proportionately greater increase of ionization than one which is not originally ionized we easily see that the meteoric impact, instead of producing uniform ionization, will tend to accentuate the ionization maxima E_1 and E_2 which are already existing.

ACKNOWLEDGMENTS.

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A NOTE ON THE CRYSTAL STRUCTURE OF SOLID H₂S.

By S. C. SIRKAR,

AND

J. GUPTA.

ABSTRACT. An attempt has been made to determine the positions of hydrogen atoms in the unit cell of solid H_2S by correlating the results of investigation of the Raman spectrum with those of the X-ray analysis of the crystal. It is pointed out that the molecule is not linear in the solid state as concluded by previous workers from results of X-ray analysis, but it is bent having the angle between the two S-H bonds equal to about 109° and the positions of the hydrogen atoms in the unit cell are exactly the same as those for the fluorine ions in the crystals of CaF_2. The space group is O_h^5.

The crystal structure of solid H_2S was investigated by L. Vegard[1] who concluded from the results of the study of the Debye-Scherrer patterns that the sulphur atoms are arranged in a face-centred cubic lattice, and from considerations of the symmetry of the unit cell he also came to the conclusion that the H_2S molecule is linear in the solid state. The study of the Raman spectrum of solid H_2S by the present authors,[2] however, revealed the fact that the H_2S molecule is not linear in the solid state but the angle between the two S-H bonds increases to about 109° in the solid state from 90° in the liquid and gaseous states. In deriving these results, the valence force system was assumed and the approximate formulæ

$$n_1^2 = \frac{f}{m}\left\{ p + (1-p)\cos^2 a/2 \right\} \ldots \qquad \ldots \qquad \ldots \quad (1)$$

and

$$n_2^2 = \frac{f}{m}\left\{ 1 - (1-p)\cos^2 a/2 \right\} \ldots \qquad \ldots \qquad \ldots \quad (2)$$

were used. As has been pointed out by Kohlrausch,[3] since $m^2/M(M+2m)$ is small in comparison with unity, m and M being the mass of the hydrogen and sulphur atoms respectively, the above approximate formulæ can be used in the present case. The value 108° for a calculated with the help of the above formulæ is therefore not far away from the actual value. The smaller of the two fre-

quencies into which n_1 is split up in the solid state was used in the calculations, but if the mean of these two frequencies be taken, the value of a so obtained does not differ appreciably from the tetrahedral angle. It is quite evident, therefore, that the value $180°$ for a obtained by Vegard from results of X-ray analysis is not correct. The purpose of the present communication is to point out that though no definite information regarding the positions of the hydrogen atoms in the unit cell can be obtained from results of X-ray analysis, such an information can be obtained by correlating the results with those of the investigation of the Raman spectrum.

According to Vegard the sulphur atoms of solid H_2S are arranged in a face-centered cubic lattice, the value of a being 5.76 A.U. and there being four molecules per unit cell. The co-ordinates of the sulphur atoms may be assumed to be $0\,0\,0$, $0\,\frac{1}{2}\,\frac{1}{2}$, $\frac{1}{2}\,0\,\frac{1}{2}$ and $\frac{1}{2}\,\frac{1}{2}\,0$. The positions of the eight hydrogen atoms should be such that the angle a is about $109°$. If the co-ordinates of the eight equivalent points in the space groups with face-centred cubic lattice be examined, only a few can give the value of a equal to about $109°$. But since the molecules themselves may possess at most the symmetry C_{2v}, the symmetry of the above space groups cannot be satisfied by the four molecules when these individual molecules are taken as independent groups which are to be brought into coincidence with one another by the symmetry operations. If, however, the four sulphur atoms and eight hydrogen atoms are taken into consideration separately, the hydrogen atoms may be arranged in such a way that in each of the four molecules the S-H distance is the same as in any other molecule and also the angle a is about $109°$ in all the molecules. The set of co-ordinates (8 e) given in Wyckoff's Analytical Expression of the Results of Theory of Space Group can be chosen for this purpose. The arrangement of the hydrogen atoms in that case becomes the same as that of fluorine ions in the unit cell of CaF_2. The space group then becomes O_h^5 and the co-ordinates of the hydrogen atoms are

$$\tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{1}{4}; \quad \tfrac{1}{4}\,\tfrac{3}{4}\,\tfrac{3}{4}; \quad \tfrac{3}{4}\,\tfrac{1}{4}\,\tfrac{3}{4}; \quad \tfrac{3}{4}\,\tfrac{3}{4}\,\tfrac{1}{4};$$

$$\tfrac{3}{4}\,\tfrac{3}{4}\,\tfrac{3}{4}; \quad \tfrac{3}{4}\,\tfrac{1}{4}\,\tfrac{1}{4}; \quad \tfrac{1}{4}\,\tfrac{3}{4}\,\tfrac{1}{4}; \quad \tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{3}{4}.$$

The distance S-H according to the above arrangement is about 2.5 A.U. which seems to be too large, but it depends on the value of a which as found by Vegard gives for the distance between nearest sulphur atoms a value equal to 4 A.U. which seems to be a little too large.

It was mentioned in the previous communication by the present authors [4] that the splitting up of the antisymmetric vibration ω_1 could be explained by assuming the effect of anisotropic crystalline field on this vibration and such an anisotropy might be expected in the case of a lattice other than cubic. The results of X-ray analysis were overlooked while making such a statement.

Since those results show that the lattice is a face-centred cubic one, at first sight it seems that such an anisotropic field is absent. It is possible, however, to arrange the molecules in the unit cell in such a way that during the vibration of the whole lattice, one pair of the molecules in the unit cell may be in a slightly larger crystalline field than the other. Such an arrangement is shown in figure 1. The molecules A and A' lie in planes which are at right angles to the planes of the molecules B and B'. There may be different phase relations between the vibrations of the four molecules in the lattice and thus a difference between the crystalline fields acting on the two pairs of molecules may be produced by some of these particular phase relations. For the symmetric vibration of the molecules, however, it may be seen from figure 1 that all the hydrogen atoms of the four molecules move in parallel planes and this may be the reason why there is no splitting of this vibration.

An alternative suggestion that there is only pseudo-symmetry of the hydrogen atoms and that the value of a for one pair of molecules is slightly different from that for the other pair is not tenable, because in that case the symmetric oscillation also would have been split up, but actually it is found to give a single sharp Raman line.
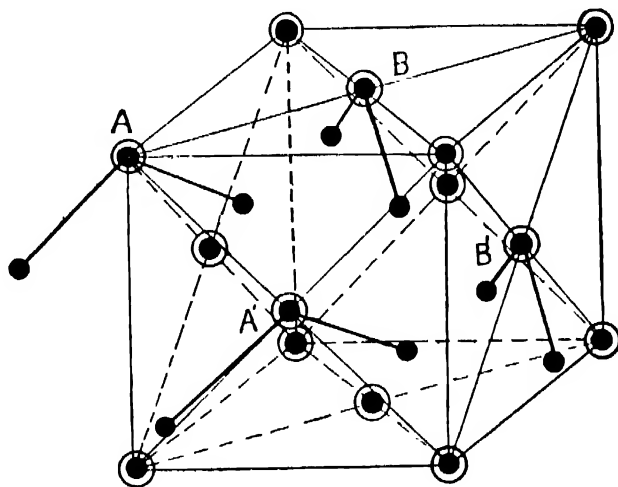
FIGURE 1.

The authors are indebted to Prof. D. M. Bose for his kind interest in the work.

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ON POSSIBLE ELECTRONIC TRANSITIONS IN Nd^{+++}IONS AND THE ABSORPTION SPECTRA OF THE SAME IN SOLUTION AND IN CRYSTALS.*

By P. C. MUKHERJI.

Plate II.

ABSTRACT. The absorption spectra of Nd^{+++} ions have been investigated over the entire range from 900 $m\mu$ to 200 $m\mu$ using solutions and crystals. In solution the intensity of light absorption has been measured with a Hilsch double monochromator. The absorption spectra in crystals have been studied over a wide range of temperature from the room temperature to that of liquid air using large single crystals of NdCl$_3$, 6H$_2$O of different thicknesses. The changes brought about by the lowering of temperature have been discussed. At low temperature the sharp absorption lines and bands of Nd^{+++} ions are distributed in groups situated fairly apart from one another. A complete list of wave-lengths and wave-numbers of these lines and bands is given. A broader classification of the absorption spectra has been included in which each group is regarded to be due to an electronic transition from the ground level to one of the other allowed inner levels of the ion. There is a fair degree of agreement between the observed and calculated intervals among the components of the multiplet levels entered in the classification. The appearance and disappearance of groups of faint lines at the temperature of liquid oxygen are discussed, and evidence is obtained of the presence of a lower excited level close to the ground level of the ions. The approximate position of this level is about 249 cm^{-1} above the basic level. This is in close agreement with the splitting of the ground level of Nd^{+++} ions in a cubic field calculated by Penney and Schlapp.

In a previous paper[†] the existence of broad and diffuse bands in the ultra-violet was reported in the case of Pr^{+++} ions in solution. Similar bands in the ultra-violet were also observed previously in Ce^{+++} ion by Bose and Datta,[1] and by Freed.[2] The broad and diffuse nature of these bands was explained as due to the transition of a 4f-electron from the basic inner level to an excited outer level of the ion. Generally speaking, however, the absorption spectra of rare earth ions in solution or in crystals consist of fairly sharp lines and bands, which resemble the spectra of gaseous atoms. They possibly arise from the so-called inner transitions between the 4f-quantum levels due to different orientations of the ' l ' and ' s '-vectors of the electrons in that shell. In the present investigations this type of absorption spectra of Nd^{+++} ions will be studied as they do not appear to have been systematically classified so far.

The investigations on the absorption spectra of the rare earth ions in the visible region started early. In this connection the work of Becquerel and de

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* Read before the Indian Physical Society on the 17th April, 1937.

† *Ind. J. Phys.*, X, p. 319 (1936).

Haas[3] is of great importance. They used the natural crystals of rare earth minerals and studied the effect of very low temperature on their absorption spectra. But these crystals usually contained a mixture of the different rare earth ions and so it was not possible for them to identify the lines and bands due to particular ions. Work on this line was later taken up by Freed and Spedding,[4] who investigated the spectra due to Gd^{+++}, Sm^{+++}, and Er^{+++} ions. They carried on a long series of investigations with large single crystals and conglomerated crystals down to very low temperatures and constructed energy level diagrams for the different ions to interpret the fine structure of their absorption spectra. The present paper contains the results of the investigations carried on with Nd^{+++} ion in solution as well as in crystals, and in the latter case at low temperatures. A broader classification of the lines and bands is also attempted here ; a more complete analysis and interpretation of the spectra will be reserved for a subsequent paper.

EXPERIMENTAL INVESTIGATIONS.

The present investigations consist of (*i*) the qualitative and quantitative measurement of the absorption of light by Nd^{+++} ions in solution over the entire spectral region from the near infra-red to the ultra-violet : (*ii*) investigation of the absorption spectra of $(NdCl_3, 6H_2O)$ crystals over a wide range of temperature, *viz.*, from the room temperature to that of liquid air.

The absorption spectra of Nd^{+++} ions in solution were investigated with Fuess spectrographs with glass and quartz prisms and lenses repectively in the visible and in the ultra-violet region. In order to photograph the near infra-red region a spectrograph with two Cornu prisms was taken and set up with the help of neon lines. Agfa Infra-red Rapid plates, sensitive up to $900\ m\mu$ were used for this part of the work. The source of light was a 250 watt straight filament high intensity lamp. Preliminary results of observation in the near infra-red and ultra-violet were published previously[5]: lafter on, these investigations have been repeated with large single crystals and at low temperatures under higher dispersion.

MEASUREMENT OF THE INTENSITY OF LIGHT ABSORPTION IN SOLUTION.

Apart from the study of the absorption spectra of solutions, the percentage of absorption of light was measured over the whole region with a Hilsch double monochromator. The experimental details of the procedure with the double monochromator is given in a paper by Datta and Deb.[6] In the visible region precisely the same arrangement was followed here, *viz.*, a potassium photo-cell and a Wulf's string electrometer were used in conjunction to measure the relative intensity of the transmitted monochromatic beam,

The solution was diluted before-hand to a suitable strength so that the maximum absorption did not exceed 50 p. c. of the incident light. The same dilution was, however, maintained throughout the experiment, in order to get an idea of the relative intensities of the different lines and bands. Finally a curve was drawn with these data, the ordinate and abscissa representing the percentage of absorption and wave-length respectively, as shown in the Figures 1, 2 and 3.
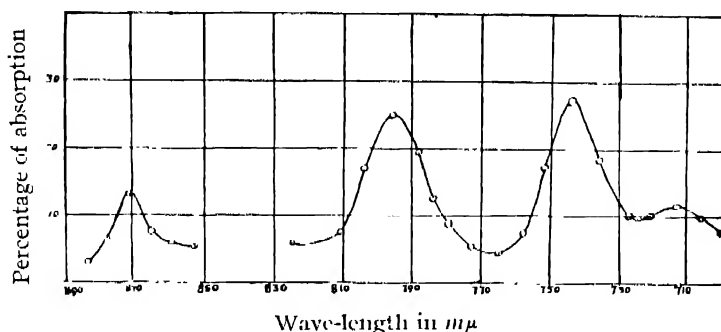
FIGURE 1.
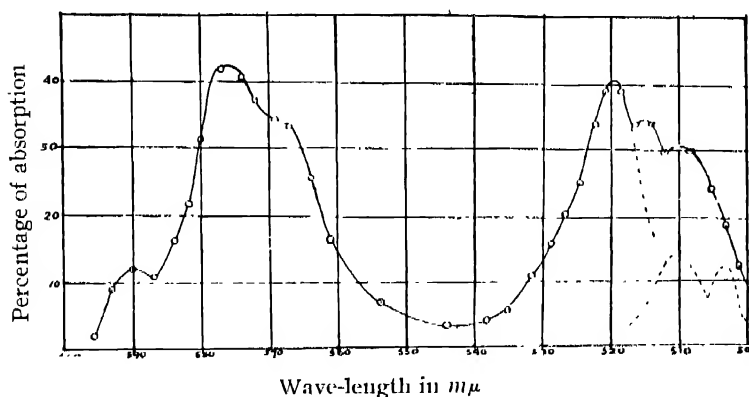
FIGURE 2.
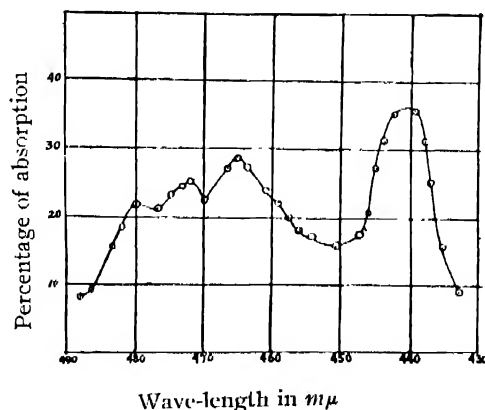
FIGURE 3.

At the extreme red end of the spectrum and in the near infra-red the K-photocell proved very insensitive and the rate of deflection of the electrometer filament became very slow. For measurement in this region, therefore, the above arrangement was replaced by a Moll's thermopile and galvanometer. As the deflection of the galvanometer was now proportional to the intensity of the monochromatic beam incident on the thermopile, it was determined accurately with a lamp and scale arrangement alternately for the solution and the solvent. This was repeated at small intervals up to 900 $m\mu$ and a curve drawn similar to that mentioned above. It was not possible to extend the investigation beyond 0.9μ as the present arrangement using glass electric bulb and glass optical parts became insensitive.

The results obtained with the monochromator are given in Table I. In Nd^{+++} ions the absorption lines and bands are distributed more or less in the form of groups, each group having a further multiplet like structure. On account of the small dispersion of the monochromator it was not possible to obtain separate peaks for each of the individual lines and bands. But corresponding to every group one crest was obtained in the curve, the highest point representing the C. G. of the group as a whole. The position of these peaks are given in the table. The ultra-violet absorption lines of Nd were very faint and so it was not possible to record them with the monochromator.

TABLE I.

	Concentration.	Thickness.	Position of aborption maxima.	Percentage of selective absorption.
I (*i*)	2% Soln.	1 cm.	8700 Å	10%
(*ii*)	,,	,,	7940 ,,	25%
(*iii*)	,,	,,	7440 ,,	28%
II (*i*)	,,	2 cm	5770, 5675 Å	40%
(*ii*)	,,	,,	5200 Å	35%
(*iii*)	,,	,,	5030, 5100 Å	12%
(*iv*)	,,	,,	4800, 4725, 4650 Å	15%
(*v*)	,,	,,	4415 Å	24%

INVESTIGATIONS AT LOW TEMPERATURE WITH *LARGE SINGLE CRYSTALS.

In order to study the absorption spectra at low temperature large single crystals of $NdCl_3, 6H_2O$ were prepared. The seeds were obtained from a solu-

tion of pure $NdCl_3$, which was saturated by evaporation on water bath and allowed to cool in a large dessicator containing a few bits of fused $CaCl_2$. After two or three days a few minute crystals were found at the bottom of the solution from which one or two small crystals with perfect surfaces were taken and allowed to grow in the saturated solution after filtering the latter very carefully. When the seeds grew to an appreciable size they were suspended inside the solution by means of fine silk threads, in order to facilitate the free growth of the faces. The crystals were allowed to grow at a very slow rate, by covering the beaker containing the solution with a paper and leaving a small aperture at the centre for evaporation. The solution was not disturbed for several days when the crystal became fairly large in size.

The crystals were, later on, ground to different thicknesses by rubbing lightly on a piece of silk moistened with a drop of distilled water. As the crystals readily absorb moisture from the air they were kept in small airtight cases. For this purpose an annular glass disc of nearly the same thickness as the crystal was taken and quartz discs were sealed on both sides with the crystal within. This was then taken inside a well fitting brass cell with openings on either sides for the passage of light. The cell is prepared from a brass rod which extends below by about one inch (see Fig. 4).
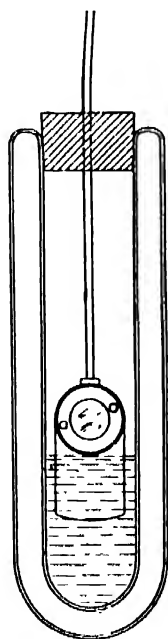
FIGURE 4.

The absorption spectra of the crystals were investigated at three different temperatures, *viz.*, room temperature, m. p. of ethyl alcohol and b. p. of liquid

oxygen. In order to cool down the crystal and maintain it constantly at the low temperature, the cooling agent say, liquid oxygen, was taken inside an unsilvered Dewar's flask and the carrier with the crystal was slowly introduced into it. The whole arrangement was kept well immersed for about 15 mins. to assure its equilibrium of temperature with the surroundings. The carrier was then raised so that the crystal was just above the surface of the boiling liquid; the lower end of the carrier, *viz.*, the solid portion dipped into the liquid and maintained the steady low temperature. By this device the crystal was surrounded by a column of the cold vapour, whereby the superposition of the diffuse absorption bands due to the cooling bath was avoided. The bath of intermediate temperature, *viz.*, m. p. of ethyl alcohol, was prepared by dropping liquid oxygen gradually on absolute alcohol till it reached a pasty viscous state prior to solidification. In practice liquid oxygen was added slightly in excess so that there was a layer of solidified alcohol above the metallic carrier.

In the visible region the spectra were photographed with a Hilger E_1-spectrograph with glass optical parts. Light from a 100 c. p. pointolite lamp was focussed on the surface of the crystal by a large condenser, and the transmitted beam was again rendered parallel by means of another convex lens placed in front of the slit of the spectrograph. This removed any non-uniformity across the length of the spectrum that often occurs in photographing with inhomogeneous crystals. Kodak supersensitive panchromatic films were used and the exposure ranged from 10 to 20 mins. at the low temperature. For the infra-red a spectrograph with two dense flint glass prisms was used. The exposure required for the Agfa infra-red plates exceeded half an hour. The suitable thickness of the crystal was here 1 mm. nearly.

In the ultra-violet region a specially constructed unsilvered Dewar's flask of fused quartz replaced the glass one. The source of continuous radiation was a hydrogen discharge tube run by a small 3 K. V. transformer at about 100 M.A current. A Hilger E_2 quartz spectrograph was used. The absorption lines were all very weak in this region, and therefore, a much thicker crystal $(t = 3$ mm.$)$ had to be used. The exposures ranged from 20 to 25 mins. A thinner crystal was also used to record the finer structure of a few absorption lines in the near ultra-violet. For this portion an ordinary tungsten filament lamp was used on account of the presence of a few emission bands in the hydrogen spectra below $300m\mu$ which persisted in spite of all precautions.

At ordinary temperature the absorption spectra consisted of narrow lines and bands distributed in groups over the entire region from $900m\mu$ in the infra-red to $240m\mu$ in the ultra-violet. With the lowering of temperature almost all the lines gained in sharpness and intensity and the bands were resolved into finer components. At the m. p. of ethyl alcohol the lines and bands were all very narrow and sharp. Further lowering produced some new results, *viz.*, at

(a)

(b)

(b')
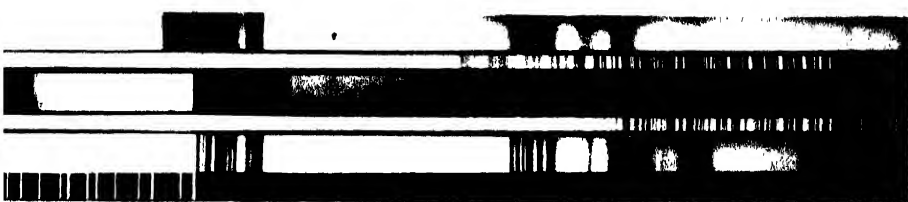
(a)

(in liquid oxygen)

(b)

(a)

(b)

(b)

(a)

Source

I Absorption spectra of (NdCl₃. 6H₂O) crystal in the near infra-red
II. ,, ,, ,, ,, in the visible region.
III. ,, ,, ,, ,, in the ultra-violet region.
(a) at room temperature. (b) at liquid oxygen temperature.
(b') at liquid oxygen temperature with different time of exposure.

liquid oxygen temperature some of the absorption lines were intensified and several faint components were added as wings to many of the so-called groups. In one particular group however an opposite effect was noticed, viz., a group of faint lines adjacent to a group of stronger lines of higher frequency became less distinct than at the alcohol temperature and could be observed only by using a thicker crystal. The components in a group appeared more dispersed, due to shift of the side components torwards red and blue. A few groups, however, did not become very sharp even at the liquid oxygen temperature. They, perhaps, required still further lowering of temperature to attain the same degree of sharpness. These characteristics are shown in Plate I, the wave-length and wave-number of the groups of lines are given in Tables II-IV (given at the end of the paper).

DISCUSSION OF RESULTS

It has been observed that lowering of temperature of the crystals brings in many interesting changes in the general appearance of the absorption spectra. At the ordinary temperature the energy levels in a solid are spread over fairly broad bands due to the superposition of the oscillations of the lattice. This produces a partial over-lapping of the consecutive energy levels and in consequence a group of fine lines is broadened into a diffuse band. It is to be expected, therefore, that at low temperature the broad bands will be resolved into sharp components and reveal the true picture of the energy levels. Further, owing to the contraction of the lattice there will be an increase in the intensity of the crystal-field which produces the splitting up of the energy levels ; so that the multiplet lines in each group will appear wider apart at low temperatures. The appearance of fainter components at low temperature is perhaps due to the violation of the selection rules under the influence of the increased electrostatic field. The disappearance of any group of lines, on the other hand, means disappearance of certain energy level at the low temperature which is possible only for a so-called lower excited level as the population there will be diminished gradually with cooling. It is found that at liquid oxygen temperature the absorption lines of Nd^{+++} with very few exceptions are all very sharp. In the following portion an analysis of these lines is given and their origin is discussed in the light of the usual theories of the spectra of rare earth ions. For a complete classification of the absorption spectra more detailed measurements with higher resolution and at still lower temperatures are necessary. Also it requires a more detailed knowledge of the effect of the crystalline field in splitting up of the energy levels of the ions, and of the selection rules governing the transitions between different term-levels, which is at present wanting.

The line emission spectra of the rare earth phosphores were widely investigated by Tomaschek.[7] He interpreted the stronger components in the spectra of Pr, Nd, Sm, etc., by transitions among the inner $4f$-levels due to the different orientations of the ' l ' and ' s ' vectors of the electrons. In ascribing the transitions he further supposed that the radiation emitted by the rare earth ions, subjected to the strong electric field in the phosphore, was quadrupole in nature. The sharp lines in the fluorescence spectra of Tb, Eu, Dy at low temperature are also regarded as due to similar transitions. It is assumed, therefore, in the reverse process, viz., absorption, the sharp lines and bands are due to inner transitions In Nd^{+++} ions containing only three $4f$-electrons the different quantum states allowed by Russell-Saunders coupling fall into two groups consisting of doublets and quartets. They are given by $^2(P, D, F, G, H, I, K, L)$ and $^4(S, D, F, G, I)$; of these $^4I_{9/2}$ evidently represents the ground state, as the term possesses minimum ' J '-value consistent with maximum ' L' and ' S '-values. The levels represented by other terms are all excited ones, according to Hund's rules, viz., (1) of all the allowed terms for the same electronic configuration those which have maximum multiplicity lie lowest ; (2) of the group of terms having the same multiplicity, the term with the largest orbital quantum number lie lowest. So that here taking the quartet levels we have $^4I<^4G<^4F<^4D<^4S$; similarly, it is among the doublet ones. Further here the multiplets being normal, the terms with smallest 'J' are lowest. At the room temperature or below the ions are mostly in the ground level and transitions from this to the other levels may be supposed to constitute the absorption lines and bands. This supposition is more or less justified by the results obtained in the measurement of absorption by the double monochromator. On comparison of the absorption curves for the solution given in Figures 1, 2 and 3 with the microphotometric records of the corresponding absorption spectra, the two sets are found to agree very closely. The slight divergences are due to the relatively small dispersion of the monochromator, which masks the finer structure of the absorption spectra. The appearance of the lines and bands in the monochromatic absorption shows that they are due to transitions from the ground level and not due to the intercombinations of the various states, which were taken into consideration by Tomaschek to account for the phosphorescence spectra.

The absorption spectra with crystals ($NdCl_3$, $6H_2O$) at the liquid oxygen temperature show that the sharp lines and bands are distributed in groups. The finer components inside the groups are very close to each other, while the groups themselves are far apart from one another. In this preliminary classification it will be assumed that each group is due to one particular transition between the ground state and a higher one, while the inner structure of a group is due to the splitting up of the levels in the crystalline field, on which are superposed the lattice oscillations and rotations. The centre of gravity of each, in wave-numbers

thus denotes the position of the corresponding electronic transition in the free ion. In Nd^{+++} ion several such groups of absorption lines have been recorded. It is attempted here to assign specific electronic transition to a few of these groups.

On account of the presence of strong electrostatic forces in the neighbourhood of the Nd^{+++} ions in crystals, the electronic transitions will deviate from the usual rules of selection. Following the rules of quadrupole radiation it is found that there are three possible types of changes in the different quantum numbers, *viz.*, '*l*', '*s*' and '*j*'.

(*i*) '*l*' and '*s*' may remain same in the initial and final states, so that there is only a change in the value of '*j*'. This evidently refers to the transitions to the upper states of the ground term multiplet, *viz.*, ^4I.

(*ii*) '*s*' may remain unchanged while the other two, *viz.*, '*l*' and '*j*' are altered in the transition. This will include all transitions from the basic level to the components of the other quartet levels allowed by R. S. coupling.

(*iii*) '*l*', '*s*' and '*j*' may all undergo a change in the transition. Such changes of the quantum numbers will be involved in transitions from the quartet ground level to some of the doublet levels allowed in the present case.

The transitions according to (*iii*) involve a change in multiplicity which is not so probable and therefore it is obvious that the corresponding lines will be fainter than due to (*i*) or (*ii*). In the following classification these alternative possibilities are considered but we confine ourselves to changes of '*j*' value not exceeding ± 2 in any transition.

In the present case, the transitions due to (*i*) have to be excluded. The lines and bands due to such transitions would be situated on the longer wave-length side of $1 \cdot 6\mu$ in the infra-red as the total interval of ^4I level amounts to 6530 cm^{-1}. In the present investigation lines and bands on the shorter side of $\cdot 99\mu$ have been recorded. Also Lueg[8] in his investigations in the infra-red region did not find any specific absorption due to Nd^{+++} between $.9\mu$ and 2.0μ. So that the first group of absorption lines in Table II may be taken to be the lowest frequency, on the wave-number scale, and can therefore be ascribed to the transition from the ground state to the next higher one, *viz.*, $^4I\,9/2 \longrightarrow\,^4G\,5/2$. In fact the four groups of absorption lines in the infra-red may be regarded as due to transitions to the four ^4G levels. It is required in such a case that the frequency differences between the centres of the consecutive groups should be equal respectively to the intervals between the component levels of ^4G. It is shown in Table V that there is a fair degree of agreement in the order of magnitude of the intervals. The calculations are made according to Sommerfeld's formula and Lande's interval rule, assuming $\sigma = 34$ for the rare earth ions. A few other transitions among the quartet levels are also specified for the stronger groups of lines in the visible region. The weaker groups of lines in the visible and the much weaker lines in

the ultra-violet are not yet classified. It appears likely from what has been said above that the weak ultra-violet lines originate in transitions to the doublet upper levels. Such transitions together with the corresponding intervals both calculated and observed are included in the table.

In the table the general intensity of the observed groups of lines is also specified. It is found that although there are some transitions which violate the principle of selection, the intensities of the corresponding

TABLE V.

C. G. of the groups			Intervals (observed).	Intensity (observed).	Transitions assigned.	Intervals (calc.)
I.	(i)	11,553 cm^{-1}		weak	$^4I_{9/2} \longrightarrow {}^4G_{5/2}$	
			956 cm^1			1,154 cm^{-1}
	(ii)	12,509 ,,		strong	$\longrightarrow {}^4G_{7/2}$	
			1,025 ,,			1,484 ,,
	(iii)	13,534 ,,		,,	$\longrightarrow {}^4G_{9/2}$	
			1,257 ,,			1,814 ,,
	(iv)	14,791 ,,		fair	$\longrightarrow {}^4G_{11/2}$	
II.	(i)	15,980		weak	$^4I_{9/2} \longrightarrow {}^4F_{5/2}$	
			1,140 ,,			1,154 ,,
	(ii)	17,120 ,,		strong	$\longrightarrow {}^4F_{7/2}$	
			1,780 ,,			1,484 ,,
	(iii)	18,900 ,,		,,	$\longrightarrow {}^4F_{9/2}$	
	(iv)	19,622 ,,		fair	$^4I_{9/2} \longrightarrow {}^4D_{5/2}$	
	(v) (a)	20,651 ,,	1,481 ,,	weak		1,154 ,,
	(b)	21,103 ,,		strong	$\longrightarrow {}^4D_{7/2}$	
	(c)	21,502 ,,		weak		
	(vi) (a)	22,428 ,,		,,		
	(b)	23,243 ,,		fair		
III.	(i)	24,745 ,,		weak	$^4I_{9/2} \longrightarrow {}^2II_{9/2}$	
	(ii)	28,486 ,,	5,667 ,,	fair	$\longrightarrow {}^2G_{7/2}$	5,441 ,,
	(iii)	30,412 ,,	4,563 ,,	,,	$\longrightarrow {}^2II_{11/2}$	4,452 ,,
	(iv)	33,049 ,,		weak	$\longrightarrow {}^2G_{9/2}$	
	(v)	34,201 ,,		,,	$\longrightarrow {}^2F_{5/2}$	
			4,082 ,,			3,463 ,,
	(vi)	38,283 ,,		,,	$\longrightarrow {}^2F_{7/2}$	
	(vii)	39,759 ,,		very weak	$\longrightarrow {}^2D_{3/2}$	
			2,616 ,,			2,473 ,,
	(viii)	42,375 ,,		,,	$\longrightarrow {}^2D_{5/2}$	

lines are much less as compared to those of the favoured transitions. Thus the lines with $\Delta J = \pm 2$ are in general much weaker than those with

$\Delta J = 0$ or ± 1. Further the fact that these faint lines are more prominent at the low temperature indicates that the selection rules break down to a greater extent in the increased crystalline field due to the contraction of the lattice. It has not, however, been possible to classify some of the observed groups. These possibly arise from transitions involving a greater violation of the selection rules than has been considered so far. Further it appears from the table that in the majority of cases the calculated intervals are not in close agreement with the observed ones. This may be due to an uncertainty in the value of the screening constant taken in the calculation. Gobrecht[9] has recently obtained the value of the screening constant ($\sigma = 34\cdot4$) for Eu^{+++} ions from the splitting of the ground term which is evidenced in the fluorescence spectra of the ion in the infra-red. Similar data for the Nd^{+++} ions are yet wanting and so no direct comparison could be made.

Before concluding this paper we shall deal with the appearance and disappearance of a few groups of lines at low temperature. It has been remarked that although most of them gain in sharpness and intensity with cooling, there are one or two which behave differently. Thus the weaker lines on the longer wave-length side of group II (*iii*) became sharp at the m.p. of alcohol, but they were reduced in intensity. At the temperature of liquid oxygen these lines were extremely faint and could be observed only by using a thicker crystal. This suggests that the origin of these faint lines is perhaps some excited lower level close to the basic level of the ion, where the population is very much reduced at the liquid oxygen temperature. The existence of such a level would require a constant frequency difference between each of the components of the faint group and the corresponding member of the adjacent strong group; also this sort of thing would recur in many of the groups. In Table VI it is shown that in the group referred to above there is actually a more or less constant interval.

TABLE VI·

Strong lines.	Weak lines.	Interval.
19,144 cm^{-1}	18,897 cm^{-1}	247 cm^{-4}
19,095 ,,	18,852 ,,	243 ,,
19,082 ,,	18,820 ,,	262 ,,
19,035 ,,	18,788 ,,	247 ,,
19,001 ,,	18,752 ,,	249 ,,
18,972 .,	...	...
18,940 ,,	18,691 ,,	249 ,,

The average value of the interval may be taken to be 249 cm^{-1}.

In this connection it will be interesting to compare the splitting of the ground term of Nd^{+++} ions in the crystalline field as calculated by Penney and Schlapp. [10] They worked out the case of hydrated sulphate in order to investigate the variation of their magnetic susceptibility with temperature. The field was here taken to be of cubic symmetry. In the absence of a magnetic field the ground state is split up into one single level and two doubly degenerate levels. When a magnetic field is present each of the levels is doubled and the total number of levels becomes ten. The energy values of the levels when this external field is absent are given by

$$W_1 = 20\cdot 95\ A,$$

$$W_2 = 9\cdot 11\ A,$$

$$W_3 = -19\cdot 59\ A.$$

The variation of magnetic susceptibility with temperature of these crystals was investigated experimentally by Gorter and de Haas and by Jackson. The above calculated values were in very good agreement with these experimental data assuming $A = -20\cdot 6\ cm^{-1}$ in the above formulae. According to this value of ' A ' the energy interval between the two lower levels becomes

$$W_2 - W_1 = -11\cdot 84\ A = 244\ cm^{-1}.$$

This is quite close to the energy interval between the lower excited level and the basic level obtained above. In the present investigation the anion was different, *viz.*, chloride ion. It may be regarded, therefore, that the crystalline field being primarily due to the dipole water molecules, is of cubic symmetry in both the cases and so the anions do not influence the splitting to any large extent.

In conclusion, the writer desires to express his grateful thanks to Prof. D. M. Bose for his kind interest and helpful suggestions during the progress of the work. He is also thankful to the authorities of the Bose Research Institute, for having kindly allowed him to use the Hilger E_1-spectrograph and offered all sorts of facilities.

<div align="center">

TABLE II.

</div>

Absorption lines in the near infra-red region with crystal of thickness$=$0·8 mm.

	R. T. λ(A°).	O. T. λ(A°).	ν(cm^{-1}).	Remarks.
(i)		8690·9	11,503	The diffuse band at R. T. is resolved at low temperature into three sharp lines.
	8645·7	8653·3	11,554	
		8610·9	11,610	
(ii)	8097·1	8097	12,347	
	8040·4	8041·2	12,433	
		8023·3	12,461	
		8006·3	12,487·2	
		7988·7	12,514	At low temperature a few new components are added; a few diffuse broad lines at R. T. are resolved. The group consists of very sharp, equidistant lines at O. T.
	7971·9	7971·1	12,542	
		7955·2	12,567	
	7933·6	7931·1	12,605	
		7899·4	12,655·6	
	7882	7881·8	12,684	
		7863·3	12,714	
(iii)	7548·3	7549·8	13,241·4	
	7492·5	7492·4	13,344	Three new components are added at O. T. and the rest become more sharp and intense.
	7454	7454·2	13,412	
		7414·8	13,482·5	
	7396·5	7397	13,515·3	
	7364·6	7364·8	13,574	
		7310·7	13,674·3	
(iv)		7278·5	13,737·3	
	6834·6	6835·5	14,625·5	The change is similar as in group (iii).
		6787	14,730	
		6767·3	14,773	
	6752·7	6751·4	14,807·7	
	6726·1	6726·2	14,863.	

(R.T—room temperature ; O.T.=liquid oxygen temperature.)

TABLE III.

Absorption lines in the visible region with crystal of thickness = 0.8 mm.
Lines marked with an asterisk are observed = 2 mm.

	R.T.	O.T.		Remarks.
	λ (Λ°)	λ (Λ°)	ν (cm⁻¹)	
(i)		6280.6	15,917.7	A group of sharp, weak, equidistant lines. These are very indistant at R.T.
		6267.1	15,952	
		6254.2	15,985	
		6242.4	16,015	
(ii)		6231.2	16,044	
		5964.7	16,761	
		5958.7	16,777.5	Many broad bands are resolved into sharper components at O.T. Some faint components are added. The lines and bands are strong.
	5915	5919.1	16,890	
		5909	16,918.6	
		5882*	16,996	
	One very broad band.	5874.6*	17,017.7	
	5875— —5775	5855.1	17,074.4	
		5845.6	17,102	
		5834.5	17,134.7	
		5823.1	17,168	
		5799	17,239.6	
		5777.5	17,303.7	
	5767.7	5767.3	17,334	
		5756.8	17,365	
	5739.9	5739.5	17,418	
	5720.9	5719.1	17,479	
(iii)	5360.2	5359*	18,654.6	This group may be subdivided into two; the first half consists of faint lines which grow weaker with cooling; the latter half as usual gains in sharpness and intensity.
		5348.6*	18,691	
	5334.7	5331.2*	18,752	
		5321.1*	18,788	
	5313.5	5312*	18,820	

TABLE III (*contd.*).

	R. T.	−O.T.		Remarks.
	λ (A°)	λ(Λ°)	ν(cm⁻¹)	
		5303*	18,852	
		5290·4*	18,897	
	5276·8	5278·4	18,940	
	5267	5269·4	18,972	
		5261·5	19,001	
	5252·3	5252	19,035	
		5239	19,082	
		5235·6	19,094·7	
	5224	5222	19,144	
(iv)		5175·3*	19,317	
	5165	5164·8	19,356·5	
		5139·1	19,457	
	5128	5133·9	19,473	Here the lines are slightly diffuse even at O. T. Many faint lines appeare at O. T,
		5123·4	19,513	
		5118·1	19,533	
		5106·6	19,577	
		5090·8	19,638	
		5069·6*	19,720	
		5039·7	19,837	
	5022·9	5026·9	19,887	
		5015·9*	19,931	
(v) (a)		4894·1*	20,427	
		4888·8*	20,449	The group grows at O. T. and very faint components are added as wings to both sides of the single strong line at 4841 Λ°
		4881·6*	20,479·4	
		4873·9*	20,511·7	
		4866·5*	20,543	
		4856·7*	20,584·4	
	4838·1	4840·9	20,651·6	

TABLE III (*contd.*).

	R. T.	O. T.		Remarks.
	$\lambda(\Lambda°)$	$\lambda(\Lambda°)$	$\nu(cm^{-1})$	
		4826·5*	20,713	
		4806·8*	20,798	
		4798·9*	20,832	
		4791·4*	20,865	
(b)		4773·2	20,944·5	
	4768·7	4767·2	20,970	
		4758·3	21,010	The appearance is of a so-called series lines. These
		4752·9	21,034	are sharp even at R. T. At O. T. they become sharper
	4743·5	4743·4	21,076	and some faint components appear.
	4729·4	4731·7	21,128	
	4715·5	4716·1	21,198	
	4703·4	4702·1	21,261	
		4688·8●	21,321·5	
	4679·5	4681·7	21,354	
		4673·5*	21,391·3	
		4666 *	21,425·7	
		4660·4	21,451·3	
		4651·8*	21,491	
		4647·3ᵏ	21,512	
	4638·7	4639	21,550·5	
		4617·8	21,649·3	
	4607·4	4609·3*	21,689	
		4568·5	21,883	
(vi) (a)		4474·8	22,341	
	4469·6	4468·5	22,372·6	Lines are slightly diffuse even at O. T.
	4453	4453·5	22,448	
		4449·3	22,469	
		4440·3	22,515	

TABLE III (*contd.*).

	R.T.	O.T.		Remarks.
	$\lambda(A°)$	$\lambda(A°)$	$\nu(\text{cm}^{-1})$	
(b)		4344·8*	23,009·6	
	4338·7	4336·9*	23,051·5	
		4307·2	23,210	
	4295	4295·2	23,275	
(vii)		4198·8*	23,809·6	
		4174 *	23,951	The group consists of very feeble lines observed only with a thicker crystal.
		4149·6*	24,092	
		4077·7*	24,517	
		4071·7*	24,553	
		4038·6*	24,754	
		4019·4*	24,872	
		4003 *	24,973·6	
(viii)		3619·5*	27,620	Many faint components are added as wings to the main group. The lines are sharp and fairly intense; diffuse bands are resolved into sharp components.
		3610*	27,693	
	3574·7	3577·7	27,943	
		3570	28,003	
	3561·5	3562·9	28,058·6	
		3538·2	28,255	
		3528·8	28,330	
	3516	3522·4	28,382	
		3493·4	28,617	
	3484	3488·2	28,660	
		3471·6	28,797	
		3467·5*	28,831	
		3454·4*	28,940	
		3444·9*	29,020	
		3422·1*	29,214	
		3405·8*	29,353	

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TABLE IV.

Absorption lines in the ultra-violet region with a crystal of thickness = 3mm.

	R.T.	O.T.		Remarks.
	$\lambda(A°)$	$\lambda(A^c)$	$\nu(cm^{-1})$	
(i)		3335·1	29,975	The lines are weak. The change with cooling is as usual.
		3326·9	30,049·4	
	3314·7	3317·3	30,136·4	
		3306·4	30,236	
		3300·	30,294	
		3290·4	30,382·7	
	3283·6	3281·9	30,461·4	
	3259	3262·4	30,644	
		3249·8	30,762	
		3242	30,837	
(ii)	3050·3	3051·7	32,759	
		3043·9	32,843	
	3040·5	3039	32,896	
	3016·5	3016·4	33,143	
		3007·6	33,240	
	3000·2	3002·6	33,293	
		2998·5	33,340	
(iii)		2934·1	34,072·5	
		2927·3	34,151·7	
	2921·4	2922·7	34,204·7	
		2918.9	34,249·5	
	2914·1	2912·1	34,330	
iv)		2624·7	38,087·7	Sharp, equidistant lines. A O.T. one sharp compo nent arises at the centre.
	2613·9	2614·3	38,240	
	2609	2610·3	38,298	
		2606	38,361	
	2601	2601·7	38,424·5	
		2598	38,479·7	

TABLE IV (*contd.*).

	R.T.	O.T		Remakrs.
	λ(Å)	λ(Å)	ν(cm⁻¹)	
(v)	2519	2519·2	39,683	Very weak lines, growing sharper with cooling.
	2513·2	2513·7	39,770	
	2509	2509·6	39,835	
(vi)		2369·2	42,195·4	Extremely weak—observed only at O. T.
		2349·2	42,551·6	

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CONSTITUTION OF WATER IN SOLUTIONS OF STRONG ELECTROLYTES.*—II.

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ABSTRACT. In continuation of the earlier work of the author, the following substances have been investigated with a view to determine their influence on the constitution of water in their aqueous solutions; $LiNO_3$, $LiCl$, $CaCl_2$, $CaBr_2$, $NaNO_2$, $NaClO_3$, $NaClO_4$ and $HClO_4$. The following are some of the main results observed :

(i) The Raman water-band in solutions is invariably sharper than in the pure solvent and is shifted, in general, to higher frequency.

(ii) At the same concentration of the salt solutions, there is a progressive shift in the band to higher frequency from $CaCl_2$ to $CaBr_2$ and $LiNO_3$ to $NaNO_2$, that in the case of the last named being the greatest.

(iii) The close similarity between the bands at the same water content observed with the acid solutions before is not so obvious with the salts.

(iv) The water-band in $HClO_4$ is particularly sharp and shifted most to higher frequency, while among the sodium salts studied, the band for $NaClO_4$ is the least sharp.

(v) The chlorides behave differently from the bromides.

(vi) The position of the intensity maximum of the water-band in solutions is characteristic of the anion and independent of the nature of the cation.

The above results are discussed in detail on the basis of a change in water equilibrium and of ionic hydration and explanations arrived at. In particular, it has been shown that change in water equilibrium is primarily brought about by the anion, while changes in the structure of the band due to hydration are mainly due to the cation.

I. INTRODUCTION.

In a previous communication,[1] the author has published the results of a detailed study by means of the Raman effect of the influence of a number of strong electrolytes—both acids and salts—on the constitution of water, when they are dissolved in it. Therein, it has been found that the influence of the dissolved electrolyte is to invariably sharpen the Raman band for water and shift it in most cases towards higher frequency. Further, the differences noticed in the structure of the band in the solutions of different substances when studied at the same concentration tended to disappear when the water content in them was equalized. The results obtained were discussed at length on the basis of the two possible

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causes of the change in the distribution of intensity along the Raman water-band, namely, a change in the water equilibrium between the proportions of the single $(H_2O)_1$, double $(H_2O)_2$ and triple $(H_2O)_3$ molecules assumed to exist in water, and ionic hydration of the molecules of the dissolved substance.

In the above study it has been noticed that the behaviour of substances containing the chloride ion—hydrochloric acid and lithium chloride were the only substances that could be then examined—was peculiar from that of the others, and it was, therefore, felt desirable to see whether chlorides alone or halides as a class behave in this manner by studying some more substances of this kind. Further, in order to generalize the conclusions arrived at before regarding the behaviour of strong electrolytes in their aqueous solutions, some more substances of this category have now been investigated.

Magat,[2] in a recent paper, studied the influence of certain strong electrolytes, namely some chlorides and nitrates of divalent and tetravalent elements, on the structure of the Raman water-band and found that the 3200 cm^{-1} component is, in general, weakened as compared with the second component at 3400 cm^{-1}, that its displacement primarily depends on the nature of the anion, the cation exercising little influence, and that it was small for chlorides and large for nitrates. The author is interested more with a satisfactory interpretation of the results obtained than with a mere enumeration of them, and has, in addition to chlorides and nitrates, studied other typical electrolytes under higher concentrations, the results obtained with which are described in the succeeding pages of this communication.

2. EXPERIMENTAL.

The experimental arrangement employed in the present investigations was, in most cases, that described in an earlier paper.[3] Sometimes, a number of filtering solutions had to be tried before a spectrum could be obtained without any continuous background, which was often so great in the unfiltered incident radiation as to make it almost impossible to obtain any reliable results. In this, as also in the previous study on this subject, the water-band excited by the $3650\text{-}63\lambda$ group of mercury lines was employed for reasons explained in Part I of this investigation. Further, the study was confined to those substances which dissolve to high concentrations—8N and above—as it was only then that unambiguous results as to the influence of the dissolved substance on the constitution of the solvent could be obtained. And, as very few substances dissolve to such high concentrations, the choice has to be limited only to those which are very highly soluble. Of these again, those substances which photo-chemically dissociate on exposure to the ultra-violet radiation from the mercury arc, *e.g.*, potassium iodide, and those which are naturally deeply coloured, *e.g.*, hydrobromic acid, had to be left out for obvious reasons.

3 . RESULTS .

Figure 1 gives the intensity curves of the Raman water-band excited by the 3650λ group in solutions of the two salts, lithium chloride and nitrate, when studied at the same concentration, *viz.*, 8N. The curve for the band in pure water is also given for purposes of mutual comparison. The distribution of intensity along the water-band in the two solutions and pure water is given in table I below.
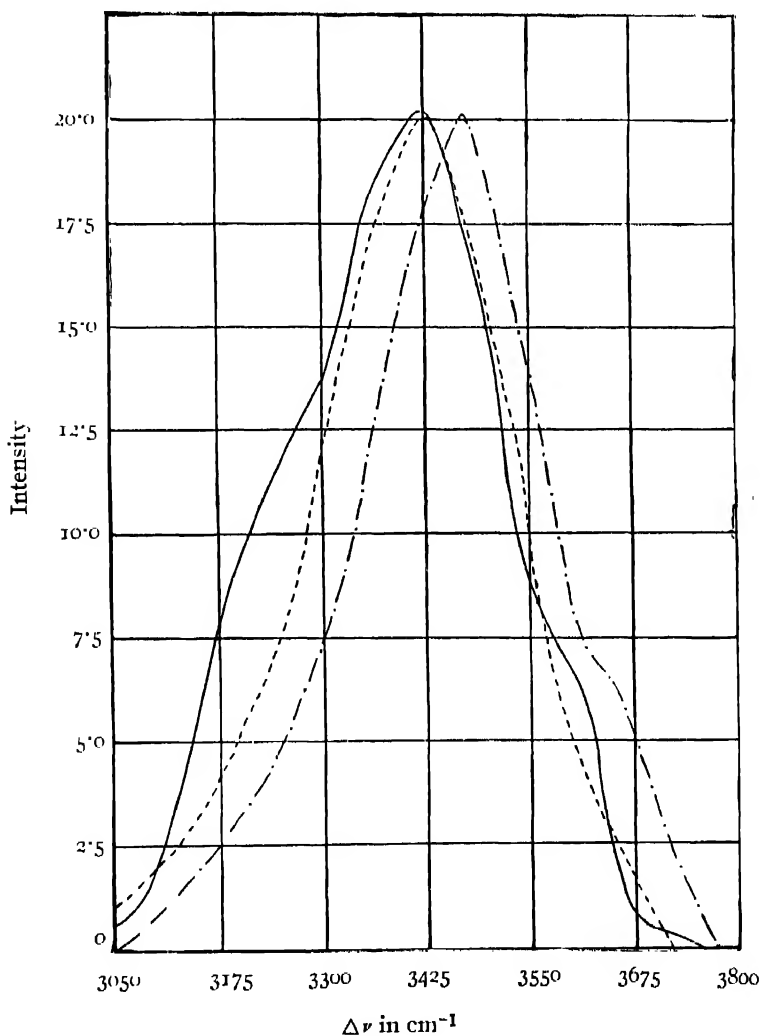
FIGURE 1

Intensity curves for the Raman-water-band in solutions of Li NO$_3$ and Li Cl at the same concentration (8N) and in pure water.

H$_2$O – – – – ;   Li NO$_3$, 8N - · · · · - - ;   LiCl, 8N - - - - - -

TABLE I.

Intensity distribution along the water-band in

1. Pure water.		2. LiNO₃, 8N.		3. LiCl, 8N.		4. LiCl, 4·2N.	
$\delta\nu$ in cm⁻¹.	Intensity.	$\delta\nu$ in cm⁻¹.	Intensity.	$\delta\nu$ in cm⁻¹.	Intensity.	$\delta\nu$ in cm⁻¹.	Intensity.
3013	0·20	3122	1·27	3051	1·03	3019	0·50
3063	0·72	3194	2·99	3110	2·12	3093	1·69
3157	6·13	3278	6·29	3175	4·12	3171	3·32
3233	9·89	3356	11·99	3253	7·85	3227	6·64
3300	13·25	3420	17·36	3331	14·67	3291	9·35
3360	18·20	3469	20·00	3406	19·47	3360	16·56
3403	19·87	3514	17·73	3429	20·02	3412	20·00
3435	20·00	3579	10·98	3443	19·10	3455	18·32
3503	14·62	3620	7·28	3492	16·30	3496	14·19
3568	7·87	3686	4·61	3543	11·56	3554	7·29
3627	5·28	3744	1·18	3619	3·92	3626	2·90
3689	0·53	...	...	3698	0·82	3670	1·42
3731	0·23	...	...	...	...	3717	0·55

The following results are noticeable from an examination of the above intensity curves :—

(i) Although the curves for the two solutions are equally broad, they are relatively shifted with respect to one another, the curve for LiNO₃ being shifted as a whole to the side of higher frequency as compared with the curves for lithium chloride and pure water.

(ii) As compared with the curve for pure water, the lower frequency portions of the two intensity curves for the salt solutions are concave in their shape, while the higher frequency branch of the curve for lithium nitrate is slightly convex in shape, the corresponding portion of the curve for lithium chloride being concave.

(iii) Although the positions of the maxima of the band in pure water and in lithium chloride solution are more or less in the same position, the lower frequency branch of the intensity curve for the latter is shifted to higher frequency as compared with that for the former and is decidedly concave in its form.

(*iv*) The bands for the solutions are sharper than that in the pure solvent—a general result noticed in the previous investigations.

The above results are largely similar to those observed with hydrochloric and nitric acids at the same concentration studied in Part I.
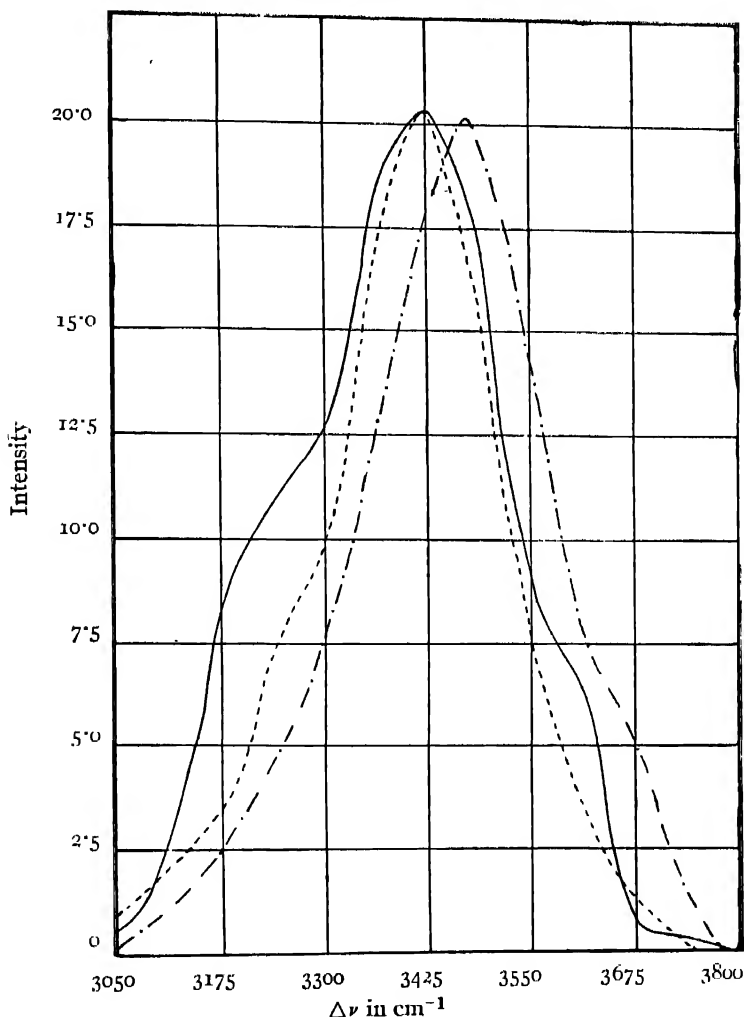
FIGURE 2

Intensity curves for the Raman water-band in solution of Li NO$_3$ and LiCl with the same water content.

H$_2$O ----- ;   LiNO$_3$, 8N· · · · · · · ·;   LiCl, 4·2N————

In figure 2 are given the intensity curves of the Raman water-band in solutions of lithium chloride and lithium nitrate having the same water content in any definite volume, together with the curve for pure water. The concentrations of LiNO$_3$ and LiCl are respectively 8N and 4·2N. The distribution of intensity along the bands is given in table I above. As compared with the curves in figure 1 at the same concentration of the solutions, the relative shift between the curves is less in this case, although still considerable, and, further, the lower

frequency branch of the curve for lithium chloride solution has developed a slight convexity at the smaller concentration. The same result is quite obvious from figure 3, in which the intensity curves for lithium chloride at the two different concentrations are reproduced together with the curve for pure water. One more interesting result that is observed from this figure is that the band at the lower concentration is slightly *narrower* than the one at the higher—an anomalous result observed before (Part I) in the case of hydrochloric acid.

In figure 4 are given the intensity curves for the four acids, hydrochloric, sulphuric, nitric and perchloric,—all at the same concentration, 8N. The values for the distribution of intensity along the band in the first three cases are taken from Part I and for the last is contained in table II.
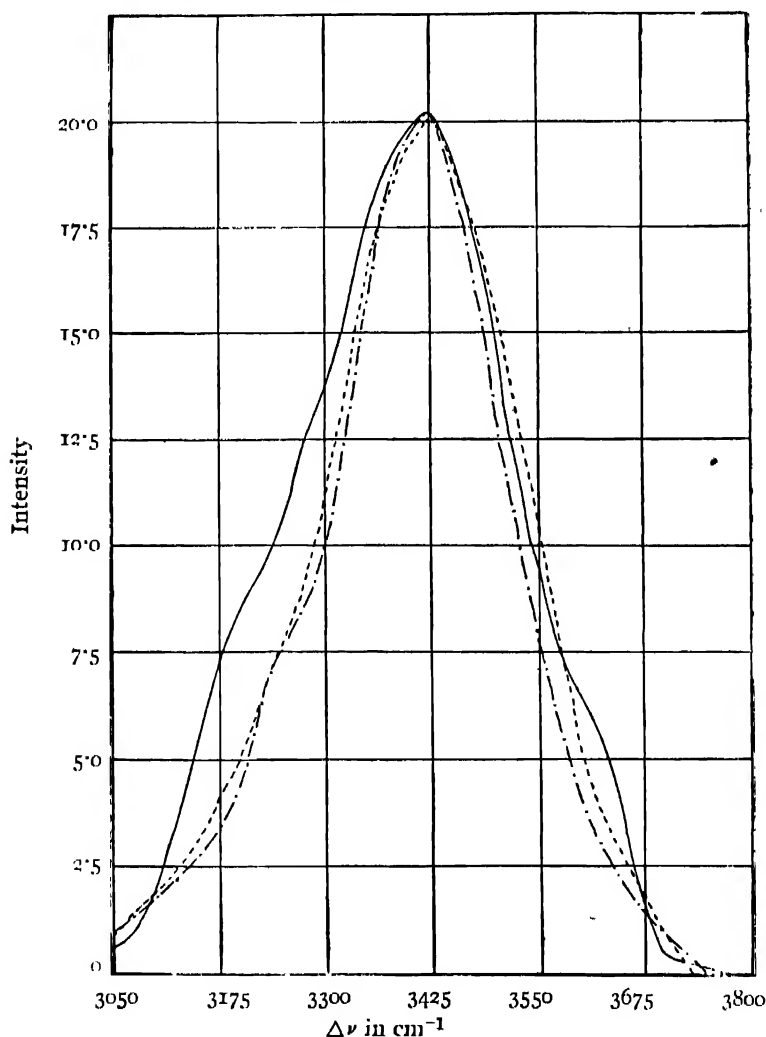
FIGURE 3

Intensity curves for the Raman water-band in solutions of LiCl at two different concentrations.

H_2O————; Li Cl, 4·2 N-··•·•·-··-; Li Cl, 8N————
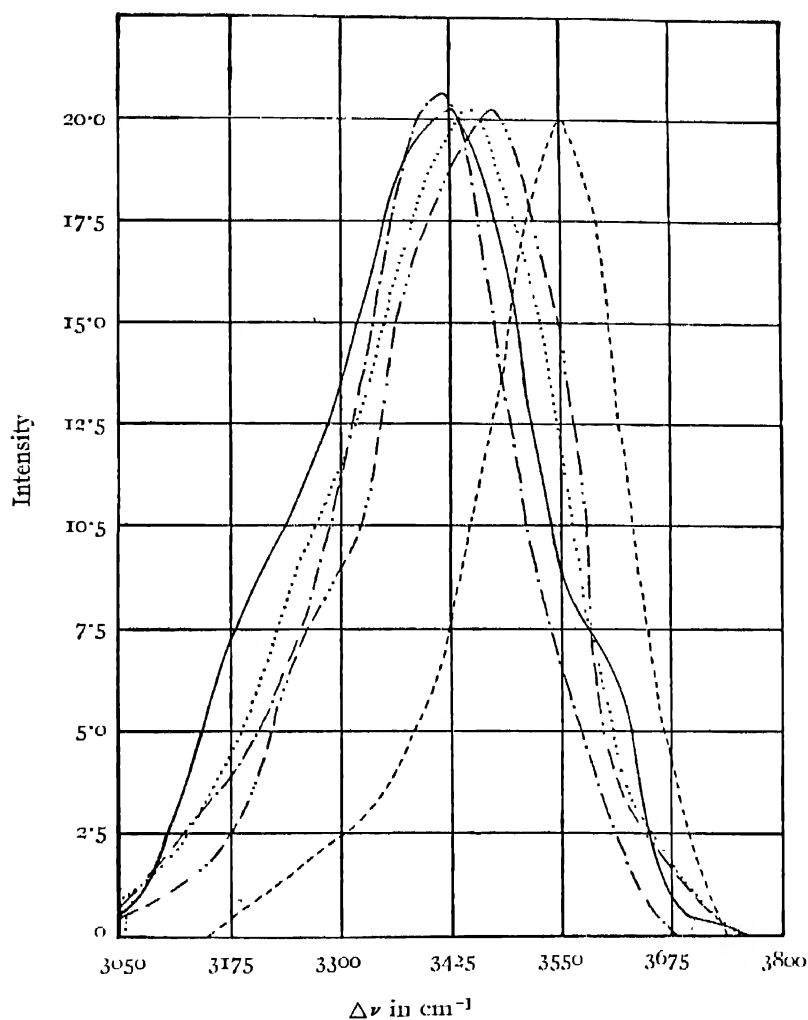
FIGURE 4

Intensity curves for the Raman water-band in solutions of *acids* at the same concentration (8N).

H₂O———; HClO₄, 8N- - - - - - - HCl, 8N- · - · - - - - -;
HNO₃, 8N- - - ... - - -; H₂SO₄, 8N...........

C. Sambasiva Rao

TABLE II.

Intensity distribution along the water-band in

1. HClO$_4$, 8N.		2. NaClO$_4$, 6 3N		3. NaClO$_3$, 7·1N		4. NaNO$_3$ 8N	
$\delta\nu$ in cm^{-1}.	Intensity.	$\delta\nu$ in cm^{-1}	Intensity	$\delta\nu$ in cm^{-1}.	Intensity	$\delta\nu$ in cm^{-1}.	Intensity
3182	0·54	3203	2·42	3139	0·38	3122	0·28
3252	1·69	3240	4·01	3211	1·30	3204	1·45
3326	2·86	3272	5 67	3274	2·46	3297	4·02
3405	6·12	3314	7·84	3324	3 89	3380	12·01
3471	12·45	3354	10·10	3382	7·37	3458	19·78
3517	17·92	3410	13·62	3448	13·83	3492	20·00
3551	20·00	3480	18·88	3488	18·57	3526	18·46
3598	16·19	3573	20·00	3523	20·00	3571	9·54
3639	8·66	3611	15·36	3564	17·94	3644	2·59
3697	2·33	3648	8·53	3622	9·33	3728	0·74
...	...	3696	3·24	3692	2·18	...	..
...	...	3730	1·68	3758	0·26	..	. .

In addition to the results noticed in the case of the first three acids as mentioned in Part I, one remarkable result observed in the case of perchloric acid here is that the water-band for the latter is extremely sharp—in fact the sharpest for all the strong electrolytes so far studied—and is shifted to a very considerable degree to the side of higher frequency, the shift being greater than in the case of any other substance studied.

Figure 5 gives the intensity curves of the water-band solutions of sodium nitrite, lithium nitrate, calcium chloride and bromide, all of them having been studied at the same concentration, viz., 8N. The curve for pure water also is reproduced for purposes of comparison. The distribution of intensity along the band in the several cases is contained in tables I and III.
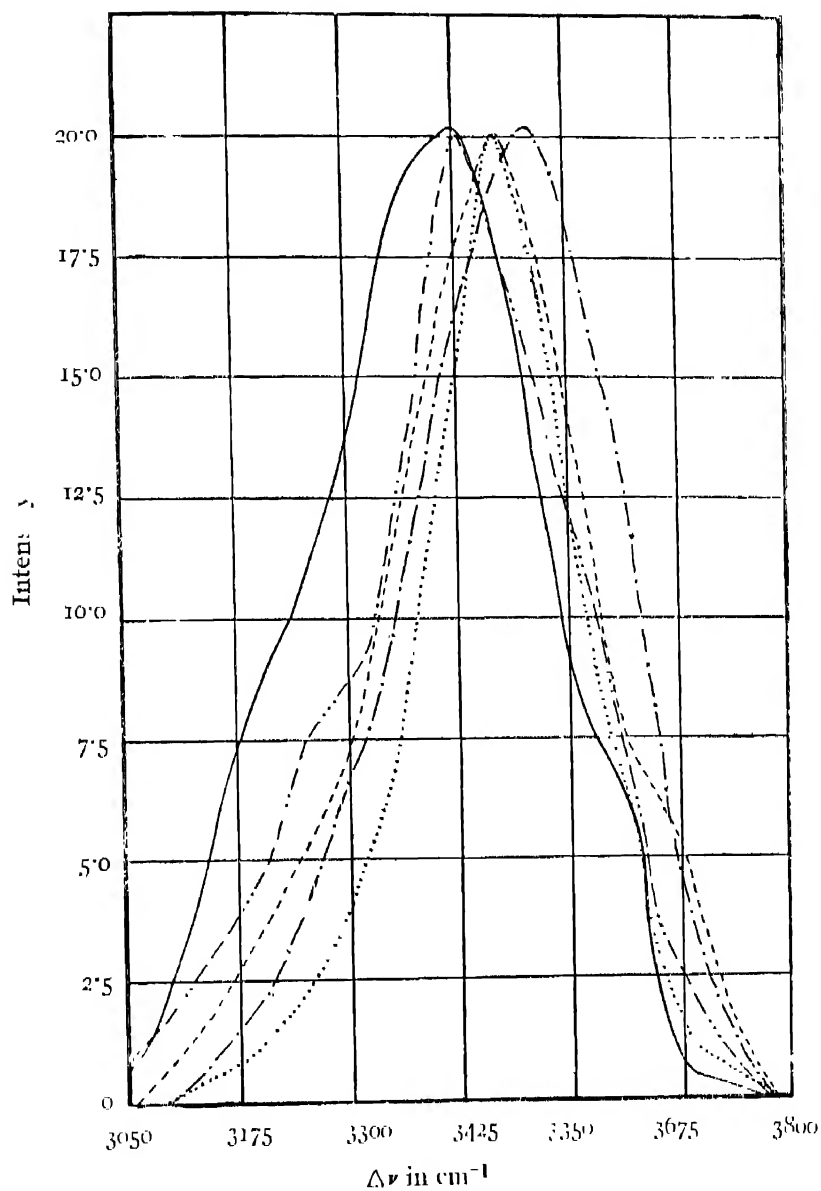
FIGURE 5

Intensity curves for the Raman water-band in solutions of *salts* at the same concentration (8N).

H_2O——; $NaNO_2$, 8N· · · · · · ·; $Li\ NO_3$, 8N———,

$CaBr_2$, 8N......; $Ca\ Cl_2$——·—· · · ——;

<div align="center">

TABLE III.

Intensity distribution along the Raman water-band in

</div>

1. NaNO₂, 8N		2. CaCl₂, 8N		3. CaBr₂, 8N.	
$\delta\nu$ in cm⁻¹.	Intensity.	$\delta\nu$ in cm⁻¹.	Intensity.	$\delta\nu$ in cm⁻¹.	Intensity.
3134	0·60	3069	1·20	3115	0·22
3202	2·10	3137	2·85	3186	0·98
3274	5·36	3201	4·65	3248	2·25
3333	8·33	3251	7·36	3293	3·64
3402	14·49	3315	9·00	3359	7·44
3471	19·04	3370	13·80	3435	16·19
3517	20·00	3407	18·09	3472	20·00
3551	18·30	3430	20·00	3523	16·29
3591	14·80	3485	16·98	3585	8·42
3625	11·61	3531	13·46	3642	3·24
3664	5·86	3587	9·68	3693	1·02
3720	1·70	3646	3·82	3742	0·42
3760	0·40	3711	1·42	...	...

The curves for the other salts studied in the present investigation (*viz.*, sodium chlorate and perchlorate) are not given in this figure, as the highest concentration at which they are available is less than 8N. From an examination of the intensity curves in figure 5, the following results are obtained :—

(*i*) As compared with the band for pure water, there is a progressive shift in the position as well as the maximum of the band towards higher frequency as we pass from calcium chloride to calcium bromide and lithium nitrate to sodium nitrite, the shift in the case of the latter being the greatest.

(*ii*) There is a pronounced convexity in shape in the lower frequency branch of the intensity curve for calcium chloride and in the higher frequency branch for lithium nitrate.

(*iii*) The band for calcium bromide appears to be the sharpest.

Figure 6 contains the intensity curves of the water-band in solutions of sodium nitrate, chlorate, and perchlorate with the same water content in any given volume, their respective concentrations being 8N, 7·1N and 6·3N. The intensity distribution along the band in the three solutions and pure water is given in tables I and II. It is seen from the figure that the bands are shifted
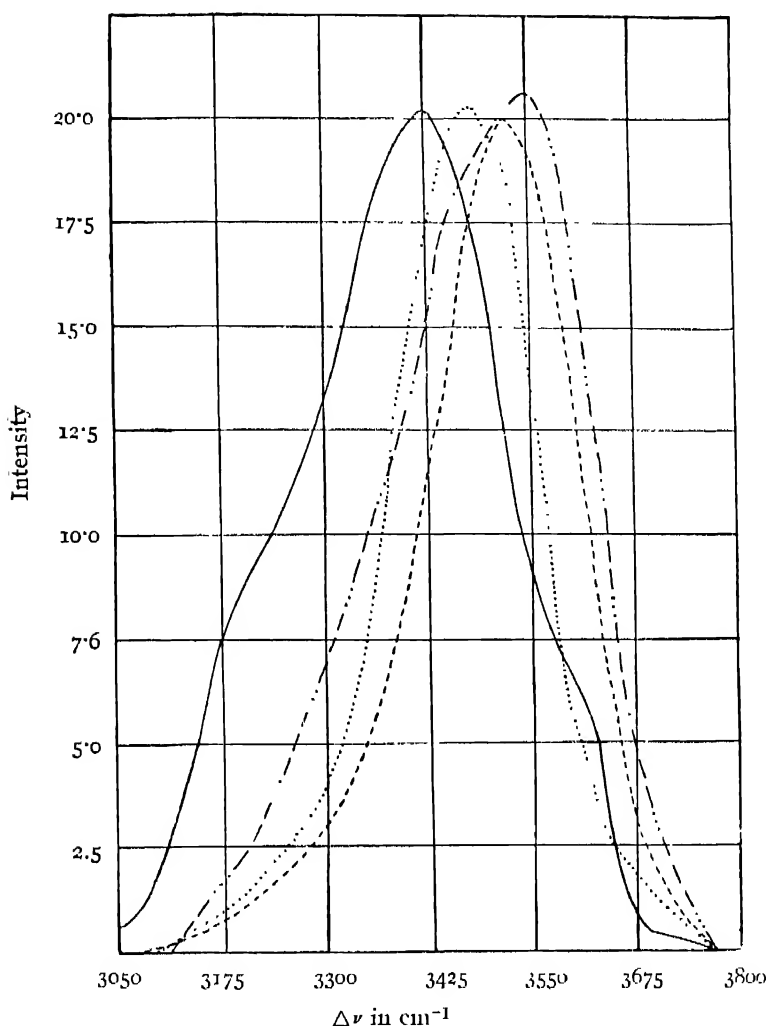
FIGURE 6

Intensity curves for the Raman water-bands in solutions of salts with the same water content.

H_2O——; $NaClO_4$, 6·3N— — —...— — —
$NaClO_3$, 7·1N - - - - - - ; $Na NO_3$, 8N.........

towards higher frequency as compared with that for pure water and relative to each other, the shift increasing from nitrate to chlorate and from chlorate to perchlorate. Further, the water-band for sodium nitrate is the sharpest and that for the perchlorate broader than the rest.

In figure 7 are given the intensity curves of the water-band in pure water and in solutions of hydrochloric acid, lithium chloride, calcium chloride and

bromide at the same concentration, *viz.*, 8N. This study is undertaken with a
view to see whether there is any close similarity in the behaviour of all the
halides as a class—a point raised in Part I of these investigations from the
anomalous behaviour of hydrochloric acid, and to study the respective influence
of the positive and negative ions on the constitution of the solvent. It is at
once seen from the figure that the curves for all the solutions containing the
chloride ion are more or less very similar, their maxima of intensity occurring
nearly in the same position for all. There are, however, certain minor differences

in the sharpness of the curves. The solution of calcium bromide, on the other hand, behaves differently from the rest in that its water-band is far sharper and is shifted considerably towards higher frequency as compared with the others, thus exhibiting a clear difference again in behaviour among the halides themselves. Of the chlorides, the curve for calcium chloride solution shows a decisive convexity in shape in its lower frequency branch, while the others are concave.
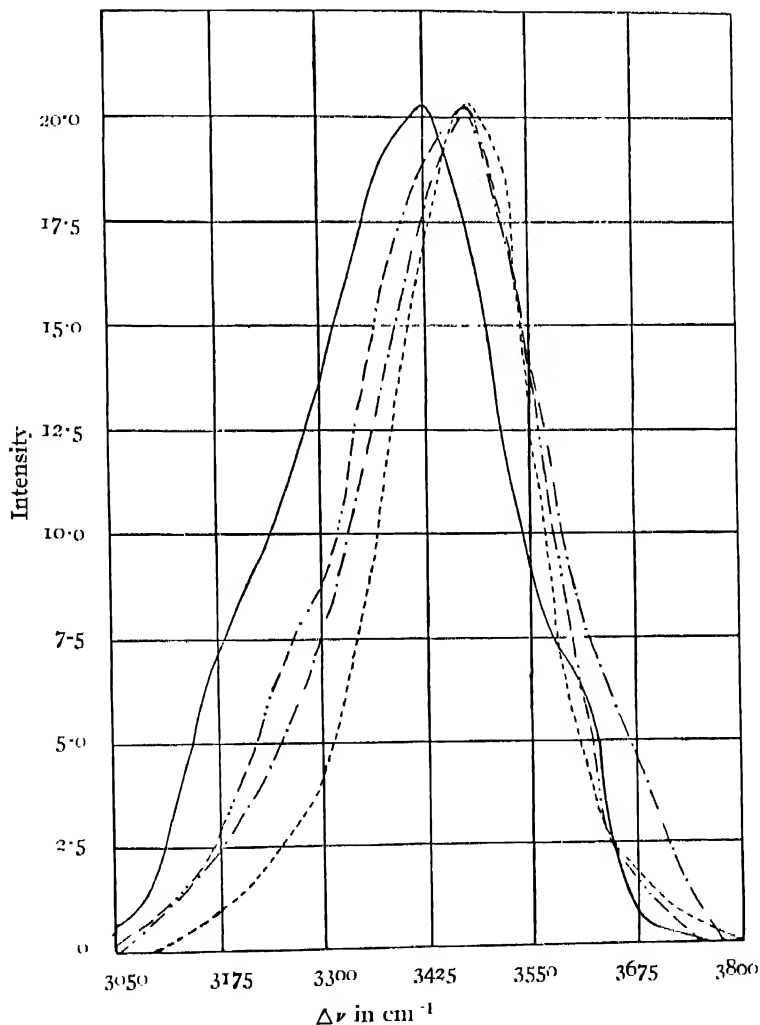
FIGURE 8

Intensity curves for the Raman water-band in solutions containing the same anion (NO$_3^-$) but different cations.

H$_2$O——— ; NaNO$_3$, 8N $\cdots\cdots$; Li NO$_3$,8N $\cdot-\cdot-\cdot$

HNO$_3$, 8N $-\cdot-\cdot\cdot-\cdot-$
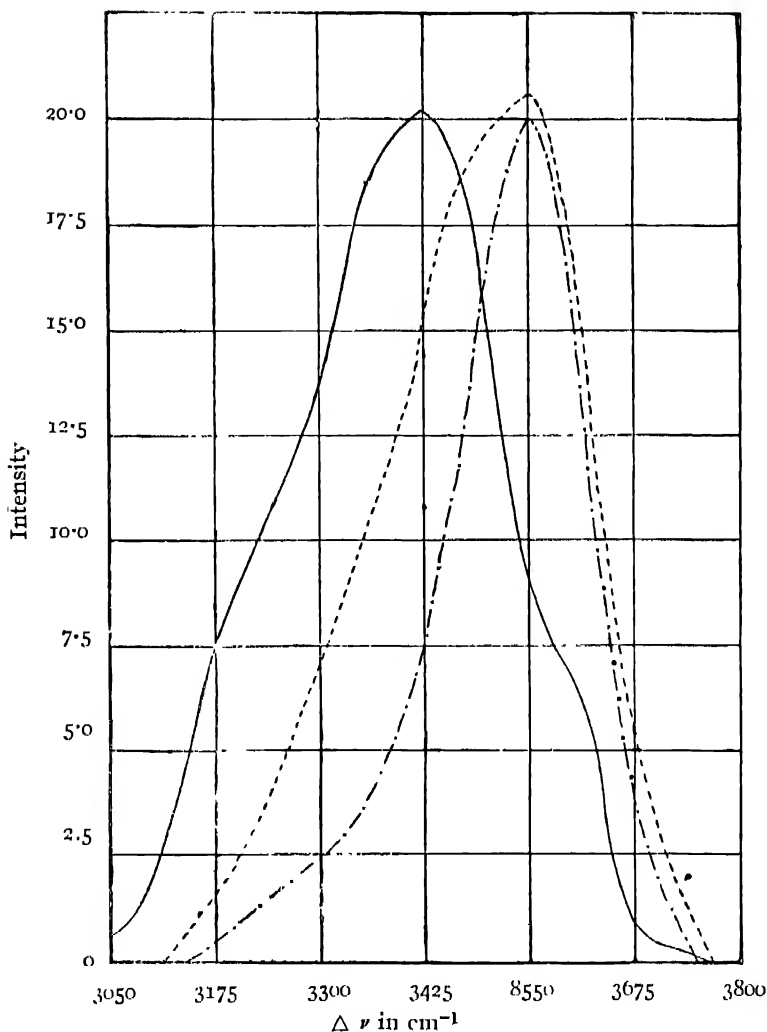
FIGURE 9

Intensity curves of the Raman water-band in solution containing

the same anion (ClO_4^-), but different cations.

H_2O——; $HClO_4$, 8N - · - · - · - · - · ; $NaClO_4$, 6·3N - - - - - -

Finally, in figures 8 and 9 are given the intensity curves of the water-band in solutions containing the nitrate ion (HNO_3, $NaNO_3$ and $LiNO_3$) and those containing the perchlorate ion ($HClO_4$ and Na ClO_4) with a view to obtain greater evidence as to the behaviour of the anion and the cation.

It is seen that, except for minor differences in the sharpness of the bands, they are similar, their maxima of intensity occurring in about the same position in each figure. This indicates that the behaviour of the water-band in these solutions is characteristic of the nature of the anion and is almost independent of the cation.

Table IV contains the positions of the intensity maximum of the water-band in the several solutions studied above.

TABLE IV

Solution.	Concentration	Position of intensity maximum of water-band.
Water	...	3424 cm [1]
LiNO$_3$	8N	3474 ,,
NaNO$_3$	8N	3480 ,,
HNO$_3$	8N	3474 ,,
HCl	8N	3425 ,,
LiCl	8N	3425 ,,
CaCl$_2$	8N	3430 ,,
CaBr$_2$	8N	3470 ,,
LiCl	4·2N	3422 ,,
HClO$_4$	8N	3550 ,,
NaClO$_4$	6 3N	3550 ,,
NaClO$_3$	7·1N	3523 ,,
NaNO$_2$	8N	3506 ,,
H$_2$SO$_4$	8N	3440 ,,

SUMMARY OF RESULTS.

The main results noticed above may be briefly summarized as follows:—

(1) The Raman water-band in solutions of electorytes is invariably sharper than that in pure water—a general result observed in Part I.

(2) Except in the case of perchloric acid and sodium perchlorate, there is an intensification of the central component of the band corresponding to double water molecules at the expense of the other two. In the case of HClO$_4$ and NaClO$_4$, however, the third component with the higher frequency shift corresponding to single molecules appears to predominate.

(3) At the same concentration, the intensity curve for LiNO$_3$ is relatively shifted to higher frequency as compared with that for LiCl, the lower frequency branches of both the intensity curves being definitely concave in shape as compared with that for pure water which is convex. The higher frequency

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branch of LiNO₃ is, however, slightly convex, while that for LiCl is concave.

(4) The water-band in solutions of lithium chloride is slightly narrower at the lower concentration than at the higher—an anomalous result formerly noticed in the case of hydrochloric acid.

(5) In the case of the salts at the same concentration, there is a progressive shift towards higher frequency as we pass from calcium chloride to calcium bromide and lithium nitrate to sodium nitrite, the shift in the case of the last being the greatest.

(6) Of the salts, the water-band in the case of calcium bromide appears to be the sharpest.

(7) There is a pronounced convexity in the shape of the intensity curve for calcium chloride on the side of lower frequency and towards higher frequency for lithium nitrate.

(8) The observed similarity in and blending together of the intensity curves of the water-band in solutions of the acids as described in Part I are not so obvious with the salts herein studied, considerable differences between the bands persisting even with the same water content.

(9) The behaviour of halides as a class is not similar, the chlorides behaving differently from the bromides.

(10) Of the sodium salts studied, the water-band in the case of the perchlorate appears to be the broadest.

(11) The position of the intensity maximum of the water-band is independent of the nature of the cation, but is characteristic of the anion.

4. DISCUSSION.

The results obtained in the present investigation, which is a continuation of the work published earlier in Part I, seem to be capable of a satisfactory interpretation on the same lines as before, namely, as the cumulative effect of a change in water equilibrium between the proportions of the single (H_2O), double (H_2O)₂ and triple (H_2O)₃ molecules, and of the hydration of the ions of the molecules of the dissolved substance.

Whereas the former work was primarily concerned with a study under different conditions of the influence of the three mineral acids, besides a few salts, on the constitution of water, the present one is mostly concerned with a study of some of the typical salts with regard to the same aspect of the problem. From a comparison of the results obtained in the two investigations, it is apparent that there are both points of similarity and dissimilarity between the acids and the salts with regard to their behaviour in aqueous solutions on the constitution of the solvent. The fact that the water-band in solutions is invariably sharper than that

in the pure liquid and that the central component due to the double molecules is intensified shows that there is no difference between acids and salts in this respect—all of them, in general, tending to increase the proportion of double molecules at the expense of the other two types, the extent to which they do, of course, varying for different substances of the same major group. In fact, in this particular aspect of sharpening the water-band in solutions, all substances—whether strong, weak or non-electrolytes seem to behave in a similar manner, as could be gathered from the previous work of the author [5] on the other classes of substances also.

From the similarity between the results obtained with addition of electrolytes to water and with change of temperature of the pure liquid, it was concluded in Part I before that the explanation of the former phenomena should, at least in part, be based upon the same lines as that put forward to explain the latter. And the latter was explained by Ramakrishna Rao[6] on the basis of the existence of three different types of molecules, namely $(H_2O)_1$, $(H_2O)_2$, and $(H_2O)_3$, the proportions of which vary with change of temperature. That such an explanation of the changes in the structure of the water-band in solutions on the basis of a change in water equilibrium is in a large measure true is also supported by the theoretical work of Bernal and Fowler[7] who arrived at a similar conclusion by a different line of attack of the problem from considerations of the viscosity of ionic solutions. They put forward the hypothesis of structural temperature in solutions, which they define as that temperature at which pure water would effectively have the same inner structure. They thus find that in all cases the effect of dissolved ions is to increase the structural temperature of water, which in terms of the author's interpretation means a shift in the band towards higher frequency, and this is exactly the experimental result observed in most cases. Further, the above authors find that the effect is much smaller for the chlorides with small ions, H^+, Li^+, Mg^{++}, than for those with large ions, and this result is again in perfect agreement with that of the author, who finds that the shift in the intensity maximum of the band is least in solutions of HCl and LiCl, the position of the maximum almost coinciding with that in pure water, while for the chloride with the larger ion, Ca^{++}, there is a small but clear shift, although not as much as for the other salts. The above result with the chlorides also agrees with the observations of Magat in the paper referred to before.

From a detailed study of the changes in the structure of the Raman band in pure water at different temperatures and in different states Ramakrishna Rao[8] allocated the three components of the band with intensity maxima at 3217 cm^{-1}, 3433 cm^{-1}, and 3582 cm^{-1}, to the three types of molecules $(H_2O)_3$, $(H_2O)_2$ and $(H_2O)_1$, respectively. On this hypothesis, the large intensity of the central component together with the diminution in intensity of the other two components of the band signifies that the proportion of the double or the so-called

'water' molecules is much more than that of the other two types. This interpretation is also supported by the observation of Ramakrishna Rao that dihydrol $(H_2O)_2$, is decidedly more stable in the liquid state as evidenced from its greater preponderance over the other two types in this state. Addition of electrolytes seems to contribute to enhance the instability of the latter types.

That the change in water equilibrium is not the only cause of the observed changes in the structure of the Raman water-band in electrolytic solutions and that hydration of the ions plays an important part as well has been shown in Part I. From considerations of the Raman effect of water of crytallization, that due to water of hydration has been deduced by the author in a former publication;[9] and that such an interpretation was correct is also supported by Bernal and Fowler in their paper referred to above, who arrive at the same result as to the close similarity between water of crystallization and water of hydration by a different line of theoretical reasoning based on the determination of ionic hydration as governed by Goldschmidt's co-ordination number. Now, the extent to which an ion can gather round it molecules of water of hydration depends primarily on its polarising power, that is, the ratio of its charge to its radius. Thus, large monovalent ions will have little effect, while small and highly charged ions will have the greatest. Bernal and Fowler infer from potential energy considerations that for univalent ions of radius greater than $1.6 \cdot \text{Å}$, no hydration can occur, while for all mono-atomic polyvalent ions hydration will always take place. Thus, the small ions, e.g., Li^+, Na^+, Mg^{++}, F^-, should be largely hydrated, while the larger ions like Rb^+, Cs^+, Cl^-, Br^-, I^-, should be least affected by water of hydration, and this is amply borne out by a lot of experimental evidence. From considerations of apparent ionic volumes and the densities of ionic solutions at great dilutions, the above authors conclude that all positive ions, except Rb^+, Cs^+, and NH_4^+, are hydrated, while all negative ions except OH^-, and F^-, are not.

This conclusion, *viz.*, that the cations are mainly responsible for the hydration effects, while the anions are for changes in the water equilibrium, is also supported from considerations of the electronic theory of valency.[10] Of the H and O atoms of the water molecule, oxygen has greater co-ordinating power and is a better donor of electrons than hydrogen is an acceptor, and the presence of a positive charge on an ion (*i.e.*, a cation) facilitates easy co-ordination between the ion and the water molecule.

Further, a few pages later, Sidgwick gives arguments from other evidences to show that, in hydrates, water molecules probably exist in pairs, thus further supporting the conclusion from Raman spectra that the enhancement of the central component of the band is due to increase in the number of double molecules in almost all solutions.

From experiments based on the transport of ions in aqueous solutions [11] the following figures were found for the relative hydrations of ions on the assumption that the number of molecules of water of hydration for H^+ is 1: K^+, 5; Na^+, 8; Li^+, 14: Cl^-, 4   Applying Stokes' law to the mobilities of ions in solutions [12] the following values are found for the relative hydrations of ions at infinite dilution: H^+, 0; OH^-, 10; K^+, Cl^- Br^-, I^-, $\frac{1}{2}SO_4^{--}$ 20; NO_3, 25; Ag^+, ClO_3^-, 35; Na^+, 70; Li^+, 150. From the above data, it is clear that the H^+ ion is the least hydrated of the smaller ions and Li^+ the most. In the case of the H^+ ion, its abnormally high mobility must also be attributed, at least in part, to its low hydration.

From the foregoing considerations, it is now easy to explain the results herein obtained with regard to the changes in the structure of the water-band in aqueous electrolytic solutions. In the case of the acids studied in Part I, it was found that, at the same water content, the intensity curves of the water-band in the different solutions became very similar in shape and position, the differences noticed at the same concentration of the solutions having disappeared to a very appreciable degree. This was taken as strong evidence in favour of the view expressed that the change in water equilibrium is the main factor contributing to the observed results in these solutions. In the case of the salts, however, both in the present investigation as well as in the previous one, considerable differences persisted even when the water content in them was equalized. These phenomena are easily intelligible when one considers the fact that, in the case of the acids, the *sparsely* hydrated H^+ ion is common to all of them, while the negative ion is generally hydrated to a negligible degree or not at all. Thus, the deciding factor in this case is the change in water equilibrium, and when the water content is equalized it is but natural that the water-band in the several acid solutions should be largely similar. In the case of the salts, however, the anions as well as the cations are different and almost all the positive ions studied (Li^+, Na^+, Ca^{++}) are largely hydrated to different degrees, the hydration in the case of Li^+ being highest. Thus in these cases, in addition to change in water equilibrium, hydration of the ions plays an equally important role, and, as it is widely different for the different ions, it is no wonder that considerable differences in the structure of the water-band persist even when the water content is equalized.

The result, that the intensity curves for lithium chloride and nitrate at the same concentration (Fig. 1) are equally broad is thus due to the large hydrating power of the common cation, Li^+, while the relative shift to higher frequency of the curve for lithium nitrate, together with the slight but definite convexity in the shape of the higher frequency branch of the intensity curve connotes that the proportion of triple molecules is considerably less and that of the single greater than in the chloride solution at the same concentration. As compared with pure

water, however, the proportion of the triple molecules is far less in both the solutions, as can be deduced from the decidedly concave shape and shift towards increasing frequency of the lower frequency branch of their intensity curves. The development of a slight convexity in the shape of the lower frequency branch of the intensity curve for lithium chloride at the lower concentration (4·2N) as compared with that at the higher signifies that at the greater dilution there is an increase in the proportion of the triple molecules together with the formation of the more complex hydrates, the component of the band corresponding to which is formed in the region of lower frequency.[13]

The extreme sharpness of the band for perchloric acid as compared with the other acids and its very large shift towards higher frequency indicates that the proportion of single molecules in this case is far larger than in the case of any other substance so far studied—in fact, they seem to be greater than the propor-tion of even double molecules, the proportion of the more complex triple type being negligible. Further, the remarkable sharpness of the band in this case is to be attributed to the almost negligible amount of hydration in this case as compared with the other acids and sodium perchlorate, the last of which, although containing the same anion (ClO_4^-), gives rise to a *broader* band with the same position of the intensity maximum on account of the greater hydrating power of the Na^+ ion.

In the case of the salt solutions studied at the same concentration (Fig. 5), the progressive shift to higher frequency as we pass from calcium chloride to bromide and lithium nitrate to sodium nitrite indicates a decreasing proportion of the more complex types of water molecules and hydrates in the above order, while the proportion of the triple molecules is less in all of them than in pure water, as can be seen from the diminished intensity and shift to increasing frequency of the lower frequency branch of their intensity curves. The develop-ment of a certain amount of convexity in the lower frequency portion of the intensity curve for calcium chloride perhaps denotes the presence to a larger degree of the more complex hydrates with three and more molecules of water of hydration.

The fact that the water-band in the solution of sodium perchlorate is broader than that in any of the other sodium salts studied indicates that the proportion of hydrates formed in this case is greater—an inference also supported by the well known fact that it crystallizes with water of crystallisation whereas the others do not.

Figures 7, 8, and 9 show clearly the influence of the anion and the cation on the structure of the water-band. In each figure, the maximum of intensity of the water-band falls in the same position, within the limits of experimental error, for all the solutions studied under each head, while the sharpness of the bands themselves is different for each of the solutions. From what has been discussed in the foregoing pages, the obvious explanation of these results is the following :

The position of the intensity maximum is characteristic of the negative ion or the so called anion and is independent of the nature of the cation. From the facts known from other evidences that the negative ions are, with the exception of OH^- and F^-, generally hydrated to a negligible degree, and from the above results from Raman spectra, it appears that change in water equilibrium is primarily a function of the anion. On the other hand, the widely divergent sharpness of the intensity curves in each of the above figures for solutions with the same anion, but different cations, suggests that those differences arise out of the different hydrating powers of the several cations, which are generally hydrated to a more or less appreciable degree. Thus, while changes due to water equilibrium are to be attributed to the negative ions (anions), changes in the structure of the water-band due to water of hydration are to be ascribed in the main to positive ions (cations).

In conclusion, the author desires to record his grateful thanks to Dr. I-Ramakrishna Rao for his stimulating interest and advice during the progress of the above investigation.

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GROUP VELOCITY CURVES FOR RADIO-WAVE PROPAGATION IN THE IONOSPHERE.

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AND

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(Communicated by Prof. M. N. Saha, F.R.S.).

ABSTRACT. Group velocity curves have been drawn for several different frequencies for radio wave propagation in the Ionosphere at Allahabad, showing how the velocity varies as the waves enter regions having greater and greater electron density. The effect of collisional friction has not been taken into account. Curves have been drawn for frequencies $p > p_h$, $p_L <$ $p < p_h$, $p_T < p < p_L$, $p < p_T$, we have in this case $p_T < p_L$. The boundary curves between various classes have also been illustrated. The curves show that the number of points at which group velocity becomes zero is larger than the points where refractive index becomes zero and thus they show that there is one more possible condition of reflection over and above the usually accepted ones. The reflections corresponding to the new condition in the case of short waves have been obtained in this laboratory.

1. INTRODUCTION.

The magneto-ionic theory developed by Breit, Appleton, Hartree, Goldestein and others has firmly established the fact that the magnetic field of the earth plays an important part in the propagation of electromagnetic waves through the ionosphere. Several investigators have drawn dispersion, absorption, and polarisation curves for the propagation of radio waves in the ionosphere. But it does not appear that the above-mentioned works have given an exhaustive account of all the phenomena connected with the propagation of the waves through the ionosphere. Recently R. N. Rai,[1] working in this laboratory obtained a new condition of reflection, proceeding on the supposition that radio waves are reflected only

when their group velocity becomes zero. The same result has also been obtained by one [2] of us from altogether different considerations. The new condition is

$$p_0^{\,2} = p^2 \, \frac{p^2 - p_h^{\,2}}{p^2 - p_L^{\,2}} \tag{1}$$

This condition of reflection was first experimentally observed by Messrs. Pant and Bajpai [3] and has also been subsequently verified. It has been pointed to us by Prof. M. N. Saha that this condition was also obtained by Goubau [4] in his discussion on the group velocity of the *e. m.* waves. But he does not appear to have contemplated the possibility of its actual existence. In fact in high latitudes, where p_L approaches p_h, this ray is scarcely distinguishable from the ordinary ray corresponding to the condition $p_0^{\,2} = p^2$.

As the group velocity appears to play a very important part in the propagation of radio waves, it appears to us that graphical curves showing the value of group velocity for different wave lengths and electron concentrations would serve a very useful purpose. The formula for group velocity according to Rai is

$$R = \frac{U}{C}$$

$$= \frac{(\omega^2 - 1 - A + \xi)^{\frac{3}{2}} \, [(\omega - \frac{1}{\omega})^2 - A + \xi]^{\frac{1}{2}}}{[\omega^2 - 1 - A + \xi][(\omega - \frac{1}{\omega})^2 - A + \xi] + (\omega - \frac{1}{\omega})^2 + \frac{A}{\omega^2} - \frac{\xi}{\omega^2} + \dfrac{B(\omega - \frac{1}{\omega})^2 (1 + \frac{1}{\omega^2})}{2\xi}}$$

where

$$w = \frac{p^2}{p_0^{\,2}} \,, \qquad A = \frac{p_T^{\,2}}{2p_0^{\,2}} \,, \qquad B = \frac{p_L^{\,2}}{p_0^{\,2}}$$

$$\xi = \pm \sqrt{(\omega - \frac{1}{\omega})^2 \, B + A} \,, \qquad p_0^{\,2} = \frac{4 \pi N e^2}{m} \,, \qquad p_{T,L} = \frac{c \, h_{T,L}}{m c}$$

$h_{T,L}$ =   Horizontal and vertical components of the earth's magnetic field.

e =   Charge on the electron.

m =   Mass of the electron.

c =   Velocity of light in vacuum.

p =   •Pulsatance of the wave.

U =   Group velocity of the wave.

As ξ is a two valued function, the above formula shows that for any one set of the values of N, p, h_T, h_L there are two values of the group velocity U. Hence there are in general two basic modes of propagation of e. m. waves of pulsatance p in a medium of constant electron density under the influence of a given magnetic field. The two modes are distinguished by the two values of R, the ratio of group velocity U to the velocity of light c in vacuum. R_1 will denote the mode corresponding to the value of R given by the positive sign, *i.e.*, to ordinary ray, while R_2 will denote that corresponding to the value given by the negative sign, *i.e.*, to extraordinary ray.

The physical quantities which define the medium under consideration are the electron density N, the transverse and longitudinal components of the earth's magnetic field h_T and h_L respectively and the collisional friction which, of course we are for the present neglecting. As the formula is applicable only to normally incident waves, h_T and h_L become fixed for a particular place. The only remaining variables therefore are N and p. The general curves will be a surface (R, N, p) from which we can obtain three sets of curves (R, N), (N, p), (R, p). Now we must consider as to which of these will prove to be of the greatest practical use to the investigators on the propagation of radio waves through the ionosphere. In our experiments we generally send waves of a particular frequency which, as they enter the ionosphere, pass through a medium in which the value of the electron density N gradually increases. Thus to show how the velocity of the incident waves change as they travel in the ionosphere, we have drawn only (R, N) curves for both types of propagation.

The four conditions of reflections are

$$
\begin{array}{ll}
(\alpha) & p_o{}^2 = p^2 + p p_h \\[2ex]
(\beta) & p_o{}^2 = p^2 \\[2ex]
(\gamma) & p_o{}^2 = p^2 \dfrac{p^2 - p_h{}^2}{p^2 - p_\mathrm{L}{}^2} \\[2ex]
(\delta) & p_o{}^2 = p^2 - p p_h
\end{array}
\qquad (3)
$$

It is to be noted that the condition (β) satisfies the mode R_1 and the conditions (α) and (δ), the mode R_2, but the condition (γ) can satisfy either of the two modes depending upon the frequency of transmission. When $p > p_h$ (γ) satisfies the mode R_2 but when $p < p_\mathrm{L}$ (γ) satisfies the mode R_1; but for $p_h > p > p_\mathrm{L}$ this condition is not satisfied at all (*vide* Appendix). The condition (δ) is also not satisfied for $p < p_h$.

Curves representing the variation of $p_o{}^2$ (*i.e.*, N) with p are also drawn for these different conditions.
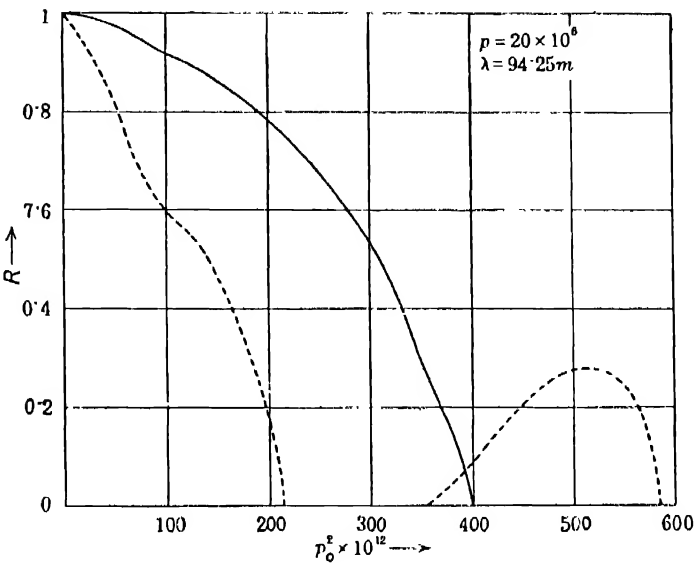
FIGURE 1.
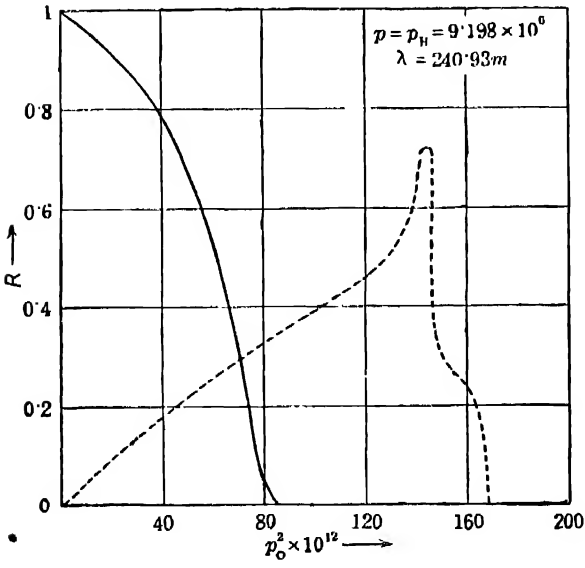
FIGURE 2.

FIGURE 3.

FIGURE 4.

$$p = 6\cdot5 \times 10^8$$
$$\lambda = 290\cdot0\,m$$

FIGURE 5.

$$p = p_1 = 6\cdot39 \times 10^8$$
$$\lambda = 294\,m$$
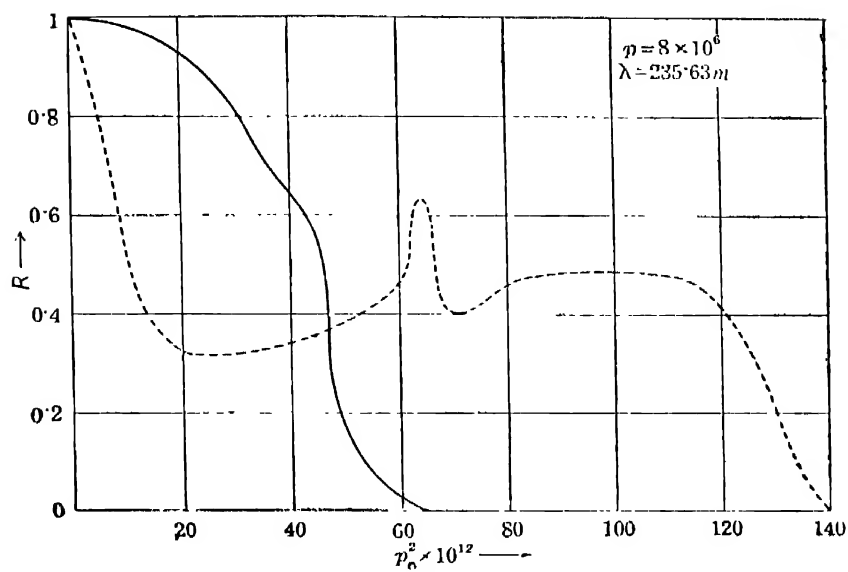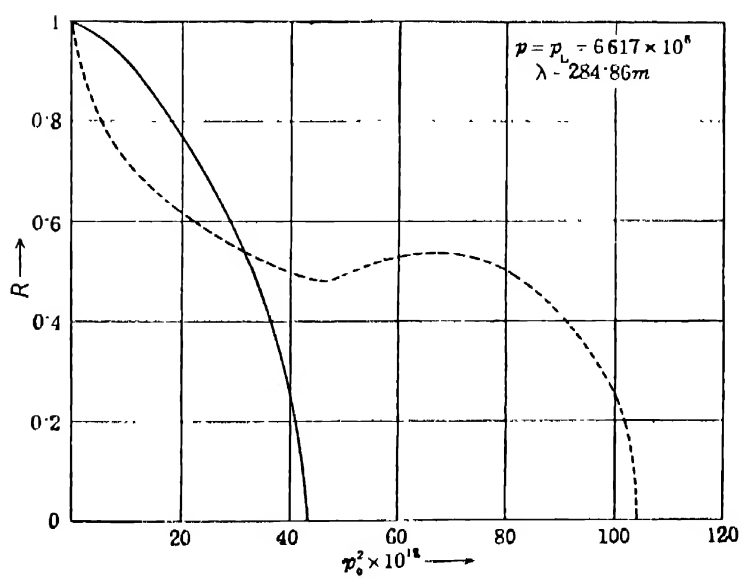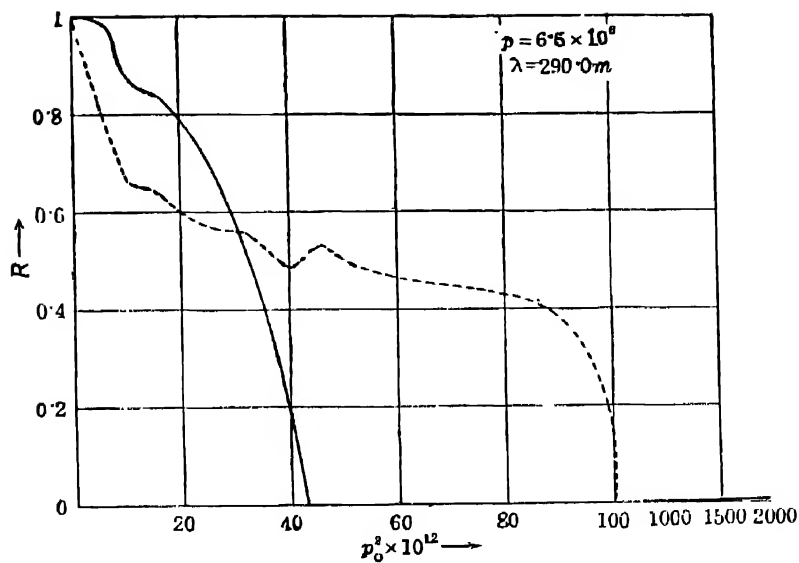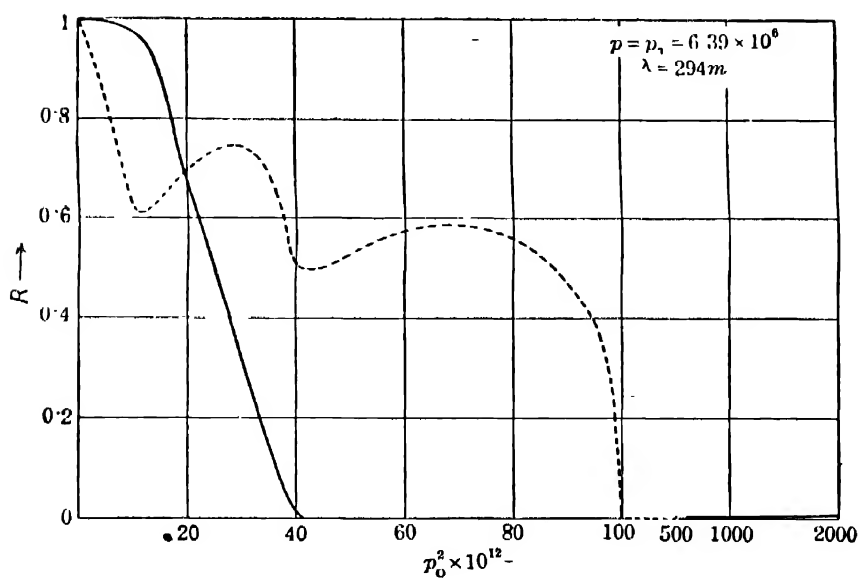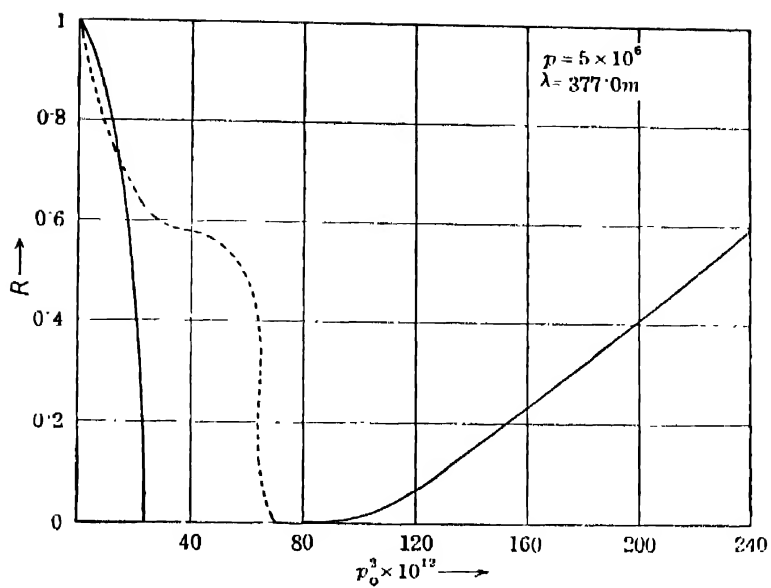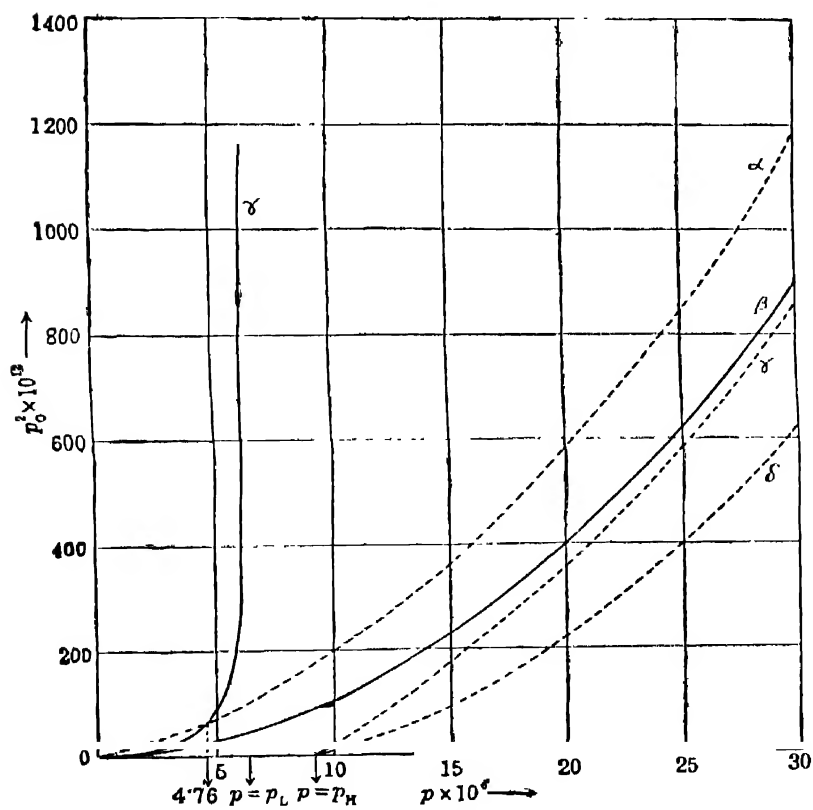
FIGURE 6.

FIGURE 7.

FIGURE 8.

NOTES ON THE CURVES ILLUSTRATED.

Velocity curves for vertical propagation of radio waves in the ionosphere at Allahabad (Lat. 25°, 25', 55″ Long. 81°, 55', 0″; $h_0 = $·373 C. G. S. Units and $h_T = 360$ C. G. S. Units) are given in the Figs. 1-7, for values of p shown in the figures. The curves corresponding to the mode R_1 (ordinary) are drawn as continuous curves, while those corresponding to R_2 (extraordinary) as dotted. Each curve represents in general the nature of variation of the group velocity of the waves, the frequency of which fall in a particular class. The angular frequencies have been classified from the point of view of the gyromagnetic frequency of the electron into classes given in columns of the table below. The chief characteristics of each particular class are also given.

Class.	Fig No.	Range of angular frequency.	Number of times group velocity is zero in mode R_1.	Number of times group velocity is zero in mode R_2.
I	1	$p > p_h$	1	3
Boundry Curve	2	$p = p_h$	1	2
II	3	$p_L < p < p_h$	1	1
Boundry Curve	4	$p = p_L$	1	1 (one zero at $p_0^2 = \infty$)
III	5	$p_T < p < p_L$	2	1
Boundry Curve	6	$p = p_T$	2	1
IV	7	$p < p_T$	2	1

(p_0^2, p) curves corresponding to the four conditions of reflections for the vertical propagation of radio waves in the ionosphere at Allahabad are given in Fig. 8. The curves α, β, γ, δ corresponds to the four conditions (α), (β), (γ), (δ), respectively. The continuous curves represent those which satisfy the ordinary ray while the dotted curves the extraordinary ray. It will be noted that the curve (γ) has split up into two parts since it does not exist for p lying between p_l and p_h.

2. DISCUSSION.

So far the investigators on the propagation of radio waves in the ionosphere have shown that for waves of frequency greater than the gyromagnetic frequency of the electrons, there are only three possible conditions of reflection. Curve number one which has been drawn for such frequencies clearly shows that there are four possible conditions of reflection—one in mode R_1 and three in mode

R_2. For waves of frequency less than the gyromagnetic frequency, only two possible conditions of reflection have been found so far, but the curves show that excepting the case of $p_l < p < p_h$ there are always three conditions of reflection. Fig. 8 shows the variation of the ionization densities with increase in frequency of the exploring waves for various conditions of reflection.

For convenience of discussion the curve can be divided into four different regions as follows:—

(a) For pulsatance between zero and $4^{\cdot}76 \times 10^6$, *i.e.*, the point at which the curve corresponding to (γ) crosses that corresponding to (α)

(b) For values of p lying between the upper limit of (a) and p_l

(c) $p_l < p < p_h$

(d) $p > p_h$.

Now so long as the frequency of the incident waves lies in the region (a), it is obvious from the curve that the maximum number of simultaneous reflections that can take place under suitable conditions is three—two in mode R_1 and one in mode R_2, as shown in Fig. 9. In general however we will have only two reflections as is usual in practice, one corresponding to (a) and

FIGURE 9.

the other mostly to (β), if the layer where (β) is satisfied is sufficiently thick. If however, the thickness of the layer where conditions (β) is being satisfied is sufficiently small compared to a wave length and the ionization gradient is quite sharp so that (γ) begins to be satisfied soon after, the waves may leak through and reflection (γ) may take place from the level where it is satisfied. In the intermediate conditions, partial reflection corresponding to both (β) and (γ) are possible and then we will have a triplet on the oscillograph. At the upper limit of this region, if reflection corresponding to (β), as discussed above, is very feeble, the reflection corresponding to both the modes will take place from the same ionization density, and if both the waves are equally retarded there will be only a single circularly polarized wave that can be received. If however there is some but small difference in the respective retardations one edge of the echo will show one type of polarization while the other edge will have the opposite polarization.

β α

FIGURE 10.

2
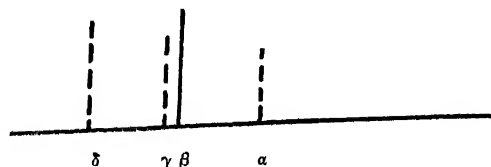
FIGURE 11.

In the region (b) there will be two reflections corresponding to (β) and (α) as shown in Fig. 10, that due to (γ) being mostly absorbed, due to great ionization density required for its reflection and consequently long path in the ionized regions and its attendant absorption.

The region (c) is quite simple, here we shall always get only two reflections one corresponding to (α) and the other to (β).

Now we come to region (d) where the greatest number of reflections is possible, for in this region all the four conditions are satisfied. The wave corresponding to mode R_1 will be reflected from the place where $(β)^1$ is satisfied, while that corresponding to R_2 will suffer its first reflection at the place where (δ) is satisfied. If however in the region where (δ) is satisfied, conditions of leakage, as discussed in (a), are also satisfied and if most of the energy leak through, the waves will suffer the principal reflection at the place where (γ) is being satisfied. If the waves are able to leak at this place also and there is sufficient energy, reflection will take place from the height where (α) will be satisfied. Now depending on the conditions prevailing in the ionosphere, the thickness of the region and ionization gradient any of these reflections may take place either alone or along with others. The oscillograph pattern can therefore in the limiting case show 4 echoes side by side thus giving rise to a quadruplet as is shown in Fig. 11.

It may be mentioned that in the region (a) and (c) the reflections corresponding to the mode R_1 will always come from a lower height than that corresponding to R_2, that in region (b) the R_2-reflection is possible from heights both less and greater than that corresponding to R_1 but the possibility of a lower height is greater especially when we advance towards the upper limit of this region, and that in region (a) there is a possibility that reflections due to R_2 may come both from heights greater and less than those due to R_1, but generally they will come from lower heights.

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APPENDIX I.

The condition (γ), *i.e.*, $p_0{}^2 = p^2 \dfrac{p^2 - p_h{}^2}{p^2 - p_l{}^2}$ is obtained from the equation 2) by putting the factor $(w^2 - 1 - A + \xi)$ of the numerator equal to zero.

Now $F = w^2 - 1 - A + \xi$

$$= \frac{p^2}{p_0{}^2} - 1 - \frac{p_l{}^2}{2p_0{}^2} \pm \sqrt{\left(\frac{p^2}{p_0{}^2} - 1\right)^2 \frac{p_l{}^2}{p^2} + \frac{p_l{}^4}{4p_0{}^4}}$$

substituting in this, the value of $p_0{}^2$ from the condition (1) we have this expression.

$$= \frac{p^2 - p_l{}^2}{p^2 - p_h{}^2} - 1 + \frac{p_l{}^2(p^2 - p_l{}^2)}{2p^2(p^2 - p_h{}^2)}$$

$$\pm \sqrt{\left(\frac{p^2 - p_l{}^2}{p^2 - p_h{}^2} - 1\right)^2 \frac{p_l{}^2}{p^2} + \frac{p_l{}^4}{4p^4}\left(\frac{p^2 - p_l{}^2}{p^2 - p_h{}^2}\right)^2}$$

$$= \frac{2p^2(p^2 - p_l{}^2) - 2p^2(p^2 - p_h{}^2) + p_l{}^2(p^2 - p_l{}^2)}{2p^2(p^2 - p_h{}^2)}$$

$$\pm \sqrt{\frac{p_l{}^4}{4p^4(p^2 - p_h{}^2)^2}[4p^2 p_l{} + (p^2 - p_l{}^2)]}$$

$$= \frac{p_l{}^2(p^2 + p_l{}^2)}{2p^2(p^2 - p_h{}^2)} \pm \left/\frac{p_l{}^2(p^2 + p_l{}^2)}{2p^2(p^2 - p_h{}^2)}\right.$$

So if $p > p_h$ F is zero when we take the negative sign and when $p < p_h$ F is zero when we take the positive sign into consideration.

Also from the condition (γ) it is clear that the value of $p_0{}^2$ is negative when $p_l < p < p_h$, which means that in this case the condition does not hold.

Therefore it is clear that condition (1) satisfies the mode R_1 when $p < p_l$, and the mode R_2 when $p > p_h$, while it does not hold when $p_l < p < p_h$.

DETERMINATION OF LATENT HEATS OF VAPORISATION OF THE SELENIDES OF CADMIUM AND MERCURY AND TELLURIDE OF ZINC FROM THE ABSORP- TION SPECTRA OF THEIR VAPOURS.

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(Communicated by Prof. M. N. Saha, F.R.S.)

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Plates III and IV.

ABSTRACT. From the study of the absorption spectra of selenides of Cd and Hg and the telluride of Zn, their heats of sublimation have been calculated with the help of Born's Cycle. Latent heats of vaporisation for CdSe, HgSe and ZnTe have been found to be 39.40, 83.23 and 61.78 respectively. The difference in the long wave-length limits of continuous absorptions for these compounds has been found to be greater than the atomic term difference $^3P-^1D$ of the electronegative element. This discrepancy have been explained with the help of Frank-Condon diagrams.

INTRODUCTION.

The selenides and tellurides of zinc, cadmium and mercury belong to the same class of diatomic compounds as the oxides and sulphides of these three elements. The absorption spectra of their oxides and sulphides were fully investigated by P. K. Sen-Gupta [1] and given suitable interpretation. In those cases where all the thermo-chemical data are available it is easy to give support to the different theories of photo-dissociation as considered in the case of monoxides and monosulphides. The absorption spectra of only three compounds out of the six are at present submitted and further investigations on the rest are in progress. For these compounds the latent heats of vaporisation have not been determined to the best of my knowledge. It is therefore thought desirable to determine this unknown quantity from the study of their absorption

spectra. It is easily done with the help of the following well-known thermo-chemical equation.
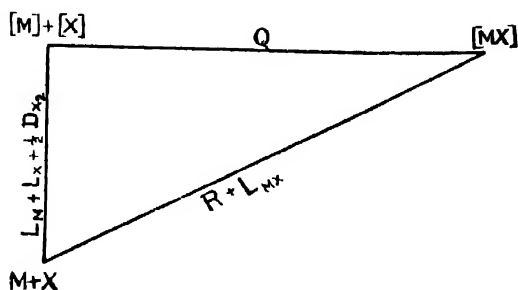
FIGURE 1.

$$L_{MX} = Q + L_M + L_X + \tfrac{1}{2} D_{X_2} - R \qquad \dots \qquad \dots \quad (1)$$

where L_{MX} = Heat of sublimation of the compound [MX]

L_M = ,, ,, ,, metal [M]

L_X = ,, ,, ,, nonmetal [X]

D_{X_2} = Heat of dissociation of X_2

Q = Heat of formation of the compound

R = Atomic heat of dissociation.

The quantity R is known from the long wave-length limit of the first continuous absorption and is connected with the wave-length λ by the equation

$$R = N.\frac{h\nu}{J} = \frac{286000}{\lambda} \qquad (2)$$

All the quantities on the right hand side of equation (1) are known and therefore heat of vaporisation of the compound can be calculated.

In analogy to other similar compounds, the selenides and tellurides may be regarded as ionic in nature, i.e., in the vapour state the compound, for example, cadmium selenide is of the type $Cd^{++}Se^{--}$. When light of a particular frequency say ν_1 falls on the vapour a simultaneous transition of two electrons from Se^{--} takes place to Cd^{++} leaving the products of dissociation in their normal states. Other processes of dissociation may also take place according to the following equations:—

$$MX + h\nu_1 = M + X(^3P) \qquad \dots \qquad \dots \qquad \dots \quad (3)$$
$$MX + h\nu_2 = M + X(^1D) \qquad \dots \qquad \dots \qquad \dots \quad (4)$$
$$MX + h\nu_3 = M + X(^1S) \qquad \dots \qquad \dots \qquad \dots \quad (5)$$

where ν_1, ν_2 and ν_3 are the frequencies of light which dissociate the compound into metal and different states of the non-metal X indicated in the above equations.

EXPERIMENT.

The new modified form of the vacuum graphite furnace is employed to vaporise the three salts for it is found to be extremely serviceable for high temperature work. The furnace in its present form has been fully described elsewhere.[2] The quickness with which it attains a steady high temperature and the ease with which it can be cleaned and manipulated make the furnace extremely serviceable for all such investigations on the absorption spectra of salts melting above a temperature of 600°C. The continuous source of light in the ultra-violet, as usual, was an air-cooled hydrogen discharge tube run by a 2 K. W. high tension transformer. In the visible region, a 40-Watt coiled-coil lamp was employed to obtain a continuous spectral background. For the ultra-violet, a small E_{31} quartz spectrograph and for the visible a constant-deviation glass spectrograph was used. Process plates were used for the ultra-violet and panchromatic plates for the visible spectra. Light from the continuous source passed through the vapour of the salt in the furnace and then allowed to fall on the slit of the spectrograph. At first absorption spectra were photographed at different temperatures. The measurement of temperature was made by a disappearing filament type of pyrometer. It was noticed that without filling the furnace with nitrogen no satisfactory results could be obtained because the vapour of the salt speedily diffused out of the silica tube placed within the current-bearing heated graphite tube. The experiments were repeated several times to obtain the best absorption at the lowest temperature for the three salts separately. After a large number of repititions of the above experiments, the following results were obtained. The positions of different cuts were located with the help of microphotograms. The spot of light was allowed to run over the continuous spectrum which was scratched at different places corresponding to the well-known lines of copper employed as the comparison spectrum. The spot of light was then run over the absorption spectrum. From these microphotometric curves, precentage absorption was plotted against wave-length. The point where this curve cut the wave-length axis gave long wave-length limit of the continuous absorption.

RESULTS.

Cadmium Selenide :—The dark reddish brown powder of CdSe when heated in vacuum from a temperature of 500°C to about 1000°C did not give any satisfactory absorption. On the introduction of nitrogen in the furnace, however, the vapour of the salt gave an absorption spectrum with two cuts with an intermediate region of retransmission as shown in the microphotogram on plate III figure 9. In figures 2 and 3 the percentage absorption curves are plotted which give the positions of the two cuts at λ 3920 and λ 2280. The resonance line of
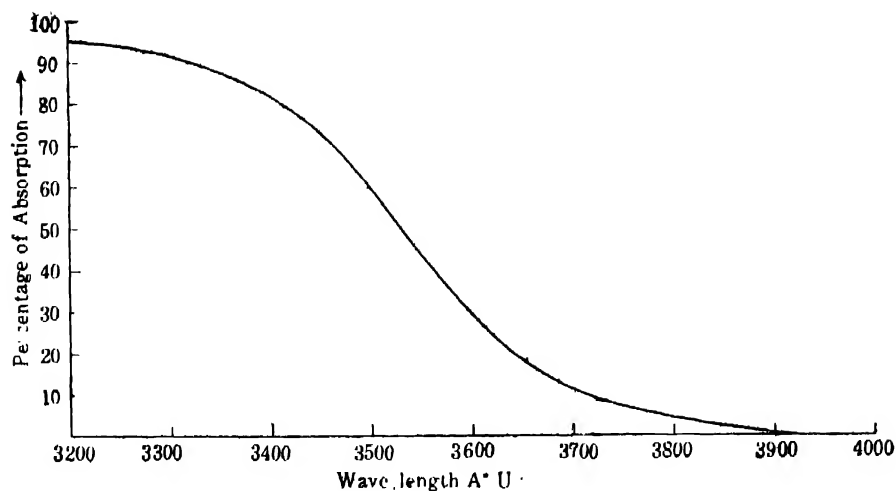
FIGURE 2.
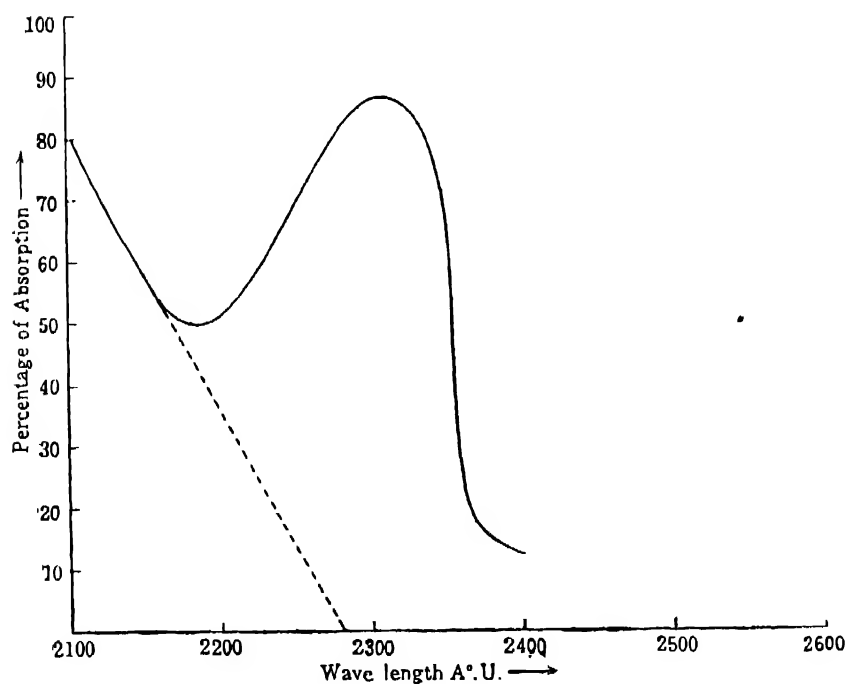
FIGURE 3.

cadmium λ 2288 appeared in nearly all the plates while the intercombination line λ 3261 did come up as it lay in the region of absorption. Usually with the continuous absorption no bands were visible but on those plates where the absorption spectrum was photographed after heating the salt for over 20 minutes, and continuous exposure to the light from the hydrogen discharge tube, Cd_2 bands first obtained by Winans, and confirmed by Sen-Gupta were also observed. Cd line
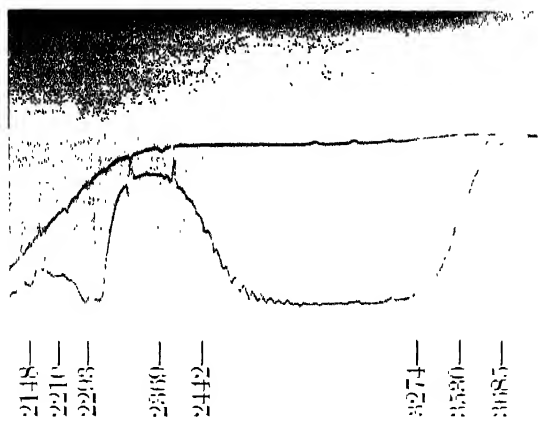
Figure 9
Microphotogram for CdSe
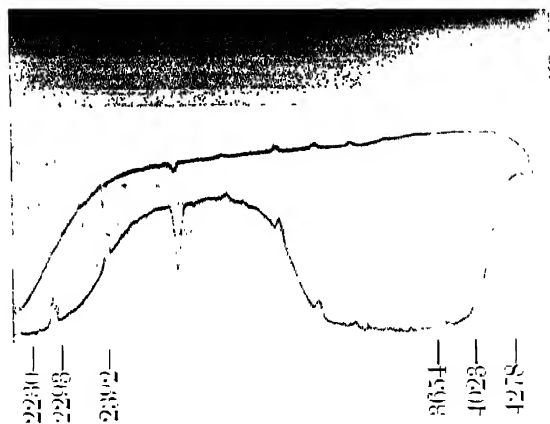
Figure 10
Microphotogram for HgSe
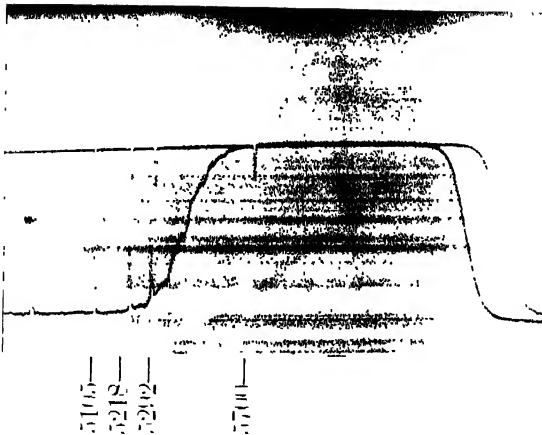
Figure 11
Microphotogram for ZnTe (visible)
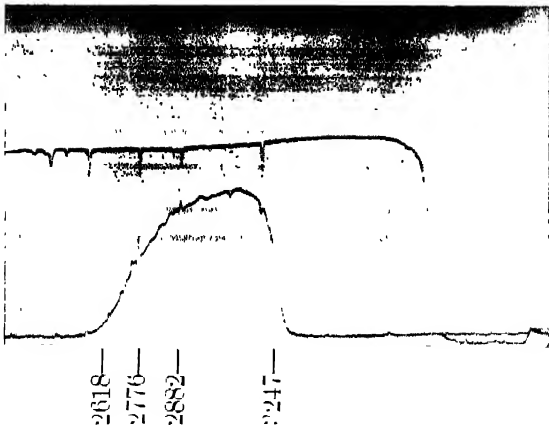
Figure 12
Microphotogram for ZnTe (ultra-violet)

λ 2288 also widened out, at higher temperatures, so much so, that it appeared like a genuine second cut on the plate. Thus in the microphotogram shown in figure 9 the apparent second cut is the broadened Cd-line λ 2288, while the real absorption due to the salt is shown in the last hump.

Mercury Selenide. The vapour of this salt gave a very good absorption spectrum at a temperature of about 820°C. Two cuts were distinctly visible together with the resonance line λ 2536 of mercury. As the temperature was increased the long wave-length limit shifted towards the red. The percentage
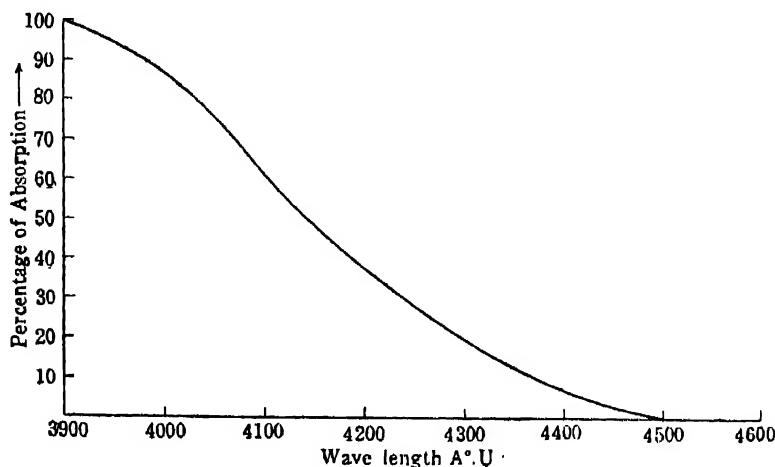
FIGURE 4.
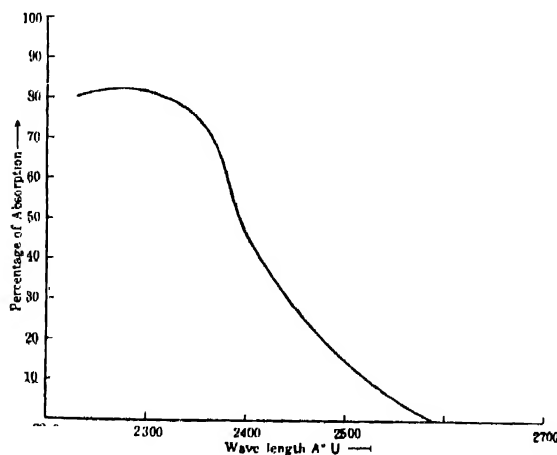
FIGURE 5.

absoption curves for the two cuts shown in the microphotogram plate III are given in figures 4 and 5. It is seen that the long wave-length limits of continuous absorptions in this case are at λ 4500 and λ 2588.

3

Zinc Telluride. The first cut with zinc telluride appeared at λ 5608 in the visible region while the second cut is located at λ3176. No absorption line or band could be found on these plates. The percentage absorption curves for the two cuts in the absorption spectrum of this compound are shown in figures 6 and 7.
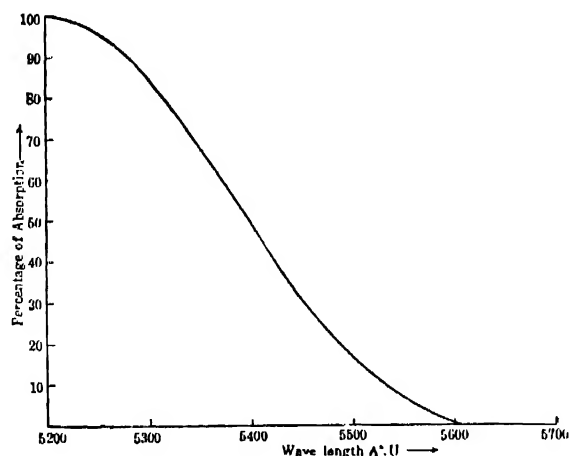
FIGURE 6.
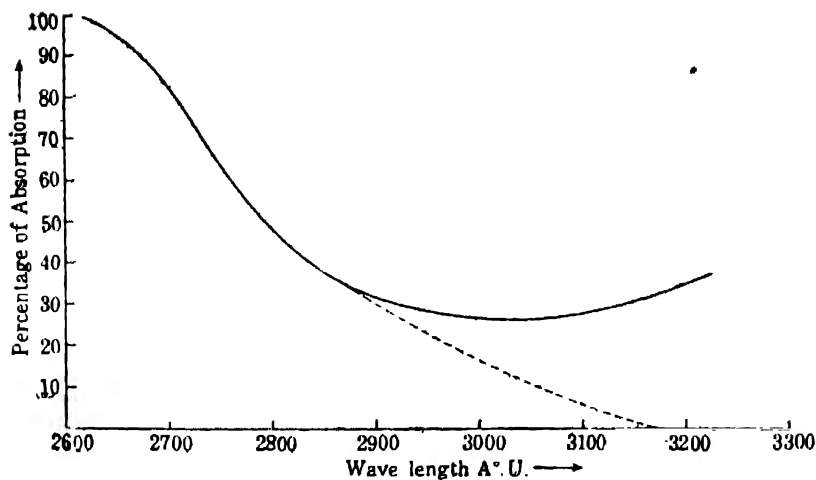
FIGURE 7.

DISCUSSION OF RESULTS.

In table 1 are given the positions of the long wave-length limits of different regions of absorption for the three salts which have been worked here,

TABLE I.

Salt.	I Absorption.		II Absorption.		$h\nu_2 - h\nu_1$.	
	λ A. U.	K. Cal.	λ A. U.	K. Cal.	K. Cal.	e. volts.
CdSe	3920	72·97	2280	125·4	52·43	2·275
HgSe	4500	63·56	2588	110·5	46·94	2·037
ZnTe	5608	51·00	3176	90·05	39·05	1·694

The last column gives the difference $h\nu_2 - h\nu_1$ between the long wave length limits of the two regions of absorption observed for these compounds. This difference has been expressed in K. Cal. as well as electron volts. If the mechanism of photodissociation corresponds to the equations (3) and (4) this difference should be equal to the atomic term difference of selenium for selenides and of tellurium for the telluride. Now, the classification of the arc spectrum of selenium has been thoroughly done by Gibbs and Ruedy [5] and Meissner, Bartelt and Eckstein [6] while atomic term values for tellurium have been investigated by Bartelt.[7] Their term values for the metastable levels $^3P_{2,1,0}$, $^1D_2$ and $^1S_0$ are given in table II together with the differences in electron volts.

TABLE II.

Element.	$^3P_{2,1,0}$	$^1D_2$	$^1S_0$	$^3P_2\text{-}^1D_2$	$^1D_2\text{-}^1S_0$
Se	78658·22 76668·73 76123·87	69082·14	56212·19	1·8	1·59
Te	72667 67960 67916	62108	49468	1·30	

The $h\nu_2 - h\nu_1$ differences for the selenides of Cd and Hg as obtained from the absorption spectra are 2·275 and 2·037 electron volts respectively. This value is much larger than the atomic term difference $^3P - {}^1D_2$. However, a suitable explanation of this discrepancy can be given as shown in the case of

monosulphides of alkaline earth elements. From the microphotometric and percentage absorption curves it is easily seen that the two regions of absorption are of the same diffuse nature, so that the potential energy curves of the two unstable states are expected to be of the form shown in figure 8.
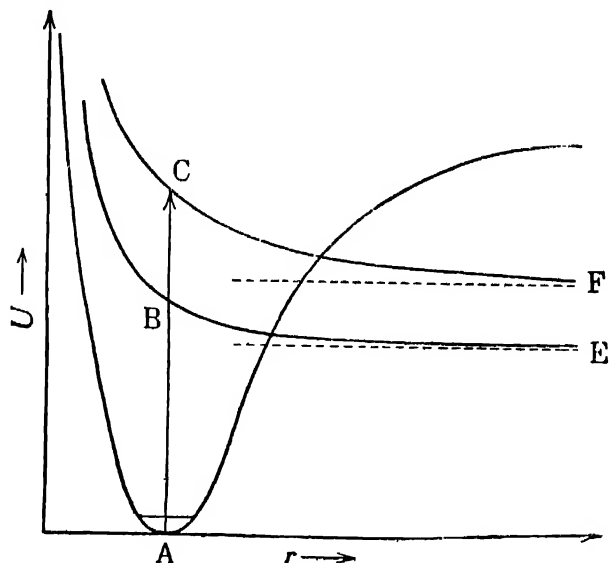
FIGURE 8.

Thus the difference BC is greater than the actual difference EF. The same explanation may also hold for the telluride of zinc where the $h\nu_2 - h\nu_1 = 1\cdot694$ while actually it ought to be $1\cdot30$.

CALCULATIONS.

As remarked earlier equation (1) furnishes us a means to determine the latent heats of these compounds spectroscopically provided R is calculated from the long wave-length limit of the first continuous absorption corresponding to the dissociation of the molecule into normal atoms. In table III are given the different thermochemical quantities involved in the calculation of L_{MX} .

TABLE III.

Salt.	Q. K. Cal.	D_{x_2} K. Cal.	L_M K. Cal	L_X K. Cal.	R K. Cal.	L_{MX} K. Cal.
CdSe	24·2	44·0	26·77	17·4	72·97	39·40
HgSe	6·3	44·0	15·53	17·4	63·56	83·23
ZnTe	31·0	37·25	31·33	13·2	51·00	61·78

Most of the above data have been collected from Landolt and Börnstein's tables. The heats of dissociation of selenium and tellurium are taken from the paper of Rosen[8] while the latent heats of vaporisation for the element Zn, Cd and Hg are those given by Egerton.[9] The last column of table III gives the latent heats of vaporisation as calculated from equation (1).

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AN X-RAY STUDY OF POTASSIUM BICARBONATE, KHCO₃

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ABSTRACT. Crystals of potassium bicarbonate $KHCO_3$ are monoclinic prismatic. The unit cell contains 4 molecules and has dimensions

$$a = 15\cdot 01 \text{ Å}; \qquad b = 5\cdot 69 \text{Å}; \qquad c = 3\cdot 68 \text{Å};$$

with an angle β of $104°30.'$

It belongs to the space group C^5_{2h} ($P2_1/a$). Relative intensity measurements suggest that the CO_3 group should be near the plane (400), having the shape and dimensions as in other normal carbonates and the potassium atom lies practically in the (010) plane.

1. INTRODUCTION.

Mooney [1] reported his preliminary X-ray investigation on the ammonium bicarbonate crystal. Out of relative intensity considerations he concluded that the CO_3 groups in the structure lie approximately in planes parallel to the a face in keeping with the findings by the magnetic method [2] and further the dimensions of the CO_3 groups are essentially the same as in normal carbonates. Later on Zachariasen [3] made a complete analysis of the sodium bicarbonate crystal. The close agreement he obtains between the observed and calculated structure-factors points out that the CO_3 groups are oriented parallel to the (101) face and here also the lattice contains CO_3 groups of the same shape and dimensions as in other carbonates. Up till now the potassium bicarbonate crystals are not known to have been studied by X-rays. As the crystals of ammonium, sodium and potassium bicarbonates form a series among the salts of the polybasic acids, an X-ray study of the $KHCO_3$ crystal in the same manner would be desirable specially with a view to investigate if the CO_3 groups here also maintain the same shape and dimensions as in others. The present paper reports a preliminary X-ray investigation of the $KHCO_3$ crystal with the help of fixed-film and moving-film cameras.

2. THE KHCO₃ CRYSTAL.

Crystals of potassium bicarbonate are described in Groth, Chemische, Krystallographie. [4] The crystal class is monoclinic prismatic with the following elements:—

$$a:b:c = 2\cdot 6770 : 1 : 1\cdot 3115 \text{ and } \beta = 103°25'$$

Merck's extra pure crystals of potassium bicarbonate were dissolved in distilled water and by very slow evaporation, lasting over several days, of aqueous solutions, single crystals of $KHCO_3$ elongated along the 'b' axis were obtained with $c\{001\}$, $r\{101\}$, $\sigma\{20\bar{1}\}$ and sometimes $a\{100\}$ bounded by $m\{110\}$.

3. UNIT CELL AND DIMENSIONS.

X-ray rotation photographs of the crystal were taken about the crystallographic a, b, c, axes in turn in a cylindrical camera of 5 cm. radius. The X-rays used were the radiations from the copper target in a shearer tube run by a transformer. The axial lengths were calculated from the mean ζ values of the layer-lines in each photograph, read with the help of Bernal Chart II[5]. Weissenberg photographs of the zero layer line about the 'b' and 'c' axes were taken in the Seemann goniometer. The dimensions of the unit cell are found to be

$$a = 15\cdot01 \text{ Å} ; b = 5\cdot69 \text{ Å} ; c = 3\cdot68 \text{ Å} ;$$

$$\beta = 104^\circ 30'$$

whence the axial ratio comes out to be

$a : b : c = 2\cdot64 : 1 : 0\cdot647$; β was directly measured from the Weissenberg photograph.

It is evident that X-ray values of the various elements of the crystal agree with Groth's values except that 'c' axial length is halved. If the density is taken as $2\cdot17$, we have 4 molecules of $KHCO_3$ per unit cell.

4. INDEXING THE REFLECTING PLANES AND THE DETERMINATION OF THE SPACE-GROUP.

In order to decipher the reflecting planes which appear in the zero layer line photograph about any crystallographic axis in the Seemann goniometer, the well-known method of graphical solution[6] was employed. In a Weissenberg photograph about the 'c' axis for example, a reciprocal lattice $a,^* b^*$ was constructed on a suitable millimetre graph-paper. Then the ξ values of the reciprocal lattice points representing the various reflecting planes were found out. The ξ values corresponding to different planes were expressed in terms of $\xi\omega$ according to the relations :—

$$\frac{\xi\omega}{2\pi r_{\text{F}}} = \frac{\theta}{180} \text{ and } 2\sin\theta = \xi$$

where θ is the Bragg angle

and r_{F} is the radius of the camera.

Then $\xi\omega$ was plotted against the angle of rotation of the camera which moves synchronously with the crystal. $\xi\omega$ markings were always made in terms of ξ in order to facilitate plotting of the reflecting planes later on. Next the interfacial angles of various planes were calculated with the help of the X-ray value of the axial ratio of the crystal in question and afterwards $\xi\omega$ (as expressed in terms of ξ) was plotted against the angle of rotation for each plane. Each reflecting plane in such a case is found to lie on two series of curves which are parabolas—one series running with (010), (110), (210), (310) etc. and the other with (100), (110), (120), (130), (140), (150), etc. The photographed film containing the diffracted spots are then superposed on the curves so drawn and the spots which lie on the intersection of two such series of curves, are easily read. In this way the following reflecting planes have been obtained and they are listed in the following table :—

TABLE.

Axial planes.	Prism planes.	Prism planes.	Prism planes.	General planes.
400 (v.s)	201 (m)	(12) $0\bar{3}$ (w)	(12) 40 (v.w)	211 (w)
600 (w.m)	$20\bar{1}$ (v.w)	(14) 02 (w)	(13) 10 (w)	$2\bar{1}\bar{1}$ (w.m)
800 (s)	$20\bar{2}$ (v.w)	(16) $0\bar{2}$ (w)	(14) 20 (w)	212 (v.w)
(10) 00 (vw)	$20\bar{3}$ (v.w)	110 (w)	(14) 30 (w.m)	222 (v.w)
(12) 00 (m)	$20\bar{4}$ (w)	120 (w)	(15) 10 (w.m)	$2\bar{2}1$ (m)
(14) 00 (v.w)	205 (w)	130 (w.m)	(15) 30 (w.m)	221 (w.m)
020 (s)	401 (v.s)	140 (w)		$4\bar{1}1$ (w)
040 (m)	401 (v.s.)	150 (v.w)		421 (w)
060 (w)	402 (w)	160 (w)		$42\bar{1}$ (w.m)
080 (v.w)	$40\bar{2}$ (m)	220 (m)		413 (v.w)
001 (w)	403 (w)	230 (v.w)		423 (v.w)
002 (m)	$40\bar{3}$ (v.w.)	240 (v w)		611 (v.w)
003 (w)	$40\bar{4}$ (w.m)	260 (v.w)		612 (v.w)
004 (v.w)	601 (v.w)	310 (w m)		613 (v.w)
005 (v.w)	$60\bar{1}$ (w)	330 (w)		621 (v.w)
	602 (v.w)	350 (w)		622 (v.w)
	$60\bar{2}$ (w.m)	420 (w)		623 (v.w)
	603 (w.m.)	440 (w)		812 (m)
	801 (s)	450 (v.w)		822 (w)

TABLE (*contd*).

Axial planes.	Prism planes.	Prism planes.	Prism planes.	General planes.
	80$\bar{1}$ (v·w)	460 (w)		
	802 (m)	510 (w)		
	80$\bar{3}$ (m)	550 (w)		
	804 (v w)	560 (v.w)		
	(10) 01 (w.m)	620 (w.m)		
	(10) 02 (v.w)	640 (v.w)		
	(10) 03 (v.w)	660 (w)		
	(10) 04 (v.w)	710 (w.m)		
	(12) 01 (w)	750 (w)		
	(12) 02 (w)	850 (v.w)		
	(12) 02 (w)	910 (w.m)		
		930 (w)		
		950 (w)		

From the table it appears that all reflexions of the type ($h\ o\ l$) are absent if h is odd, and reflexions ($o\ k\ o$) are absent in odd orders. Consequently the symmetry plane is a glide plane with a translation $a/2$, and the two-fold axis of rotation is a screw axis with a translation $b/2$. It follows therefore that the space-group is C_{2h}^5 (P 2_1/a).

5. CONCLUSION

The space-group C_{2h}^5 requires 4 asymmetric units for the unit cell. As the $KHCO_3$ crystal possesses 4 molecules per unit cell, the $KHCO_3$ molecule probably has no element of symmetry. It may be safely assumed that the CO_3 group in the $KHCO_3$ molecule has the shape of an equilateral triangle with the oxygen atoms at the corners and the carbon atom at the centre, and the potassium atom lies in a different plane. The distance between oxygen and carbon is taken to be 1.27Å. With these assumptions the analysis is in progress and unless it is complete, no definite conclusion regarding the structure can be drawn. But so far the analysis shows that in the $KHCO_3$ crystal also the CO_3 groups maintain their shape and dimensions. Strong reflexions from planes of the type (400), (401), (40$\bar{1}$) etc., suggest that the CO_3 group should be

very near the plane (400). The absence of all planes (h10) where h is even and the weak reflexions of almost all the planes ($h\,k\,o$) where ($h+k$) is odd, require that the potassium atom which is the predominant scatterer lies practically in the (010) plane. The magnetic susceptibilities [7] of single crystals of $KHCO_3$ also lead to the same configuration of the CO_3 group.

In conclusion, the author desires to express his grateful thanks to Prof. K.S. Krishnan, D.Sc. and the members of the committee of management, Indian Association for the Cultivation of Science, for providing him facilities for the work.

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ON DELAY IN TRANSMISSION THROUGH TELEPHONE APPARATUS AND NETWORK

By P. B. GHOSH, M.Sc.

ABSTRACT. The paper relates to the measurement of delays in transmission through some typical telephone apparatus and network (for instance, wave-filters, telephone transformer, repeating coils and audio-amplifier). This study has recently become important on account of growth of multiplex communication systems in which frequency band of each channel has to pass through several additional networks and is consequently liable to suffer additional delay.

Phase-shift (β) was measured by an arrangement similar to that adopted by Messrs. Hinton, Kendall and White, for telephone repeaters. Delay $\left(\dfrac{d\beta}{d\omega}\right)$ at various frequencies was obtained from phase-shift characteristics.

Measurements have shown that, in general, for individual apparatus or network the order of delay is not high and its variation with frequency is unable to cause phase distortion; but in a channel where several wave-filters (each consisting of two or more sections), transformers and amplifiers are connected in tandem with a long line circuit the total delay and its variation with frequency will affect transmission.

1. INTRODUCTION.

Study of the time factor in transmission over telephone circuit and associated apparatus, networks, etc., at terminal and repeater stations is desirable at the present moment when the trend of development is towards longer and longer connections.

On a telephone circuit having resistance, inductance, capacitance and leakance of R, L, C, and G per loop mile respectively, the phase constant is given by

$$\beta = \sqrt{\tfrac{1}{2}\left[\left\{\left(R^2+L^2\omega^2\right)\left(G^2+C^2\omega^2\right)\right\}^{\frac{1}{2}} + \left(\omega^2 LC - RG\right)\right]} \qquad \ldots (1)$$

and the velocity of propagation by

$$v = \frac{\omega}{\beta} \qquad \ldots (2)$$

On unloaded circuits either open-wire or cable, the velocity of transmission of telephone currents over line conductors is high and increase with the increase of frequency of the current to an upper limit of 186,000 miles per second. Present day loaded trunk cable circuits for moderate and long distances have velocities of the order of 10,000 and 20,000 miles per second respectively and further the

transmission velocities for the middle frequencies of the speech band (*i.e.*, 1,000 to 1,500 c.p.s.) are usually greater than those of the higher or the lower frequencies.

The effects of low velocity of transmission and its variation with frequency are discussed below with reference to transmission on long circuits.

(a) " Phase distortion " or " Transient Effect ":—

The components of different frequencies making up the speech are not all transmitted with the same velocity over the telephone circuits. In an unloaded circuit (open-wire or cable) the velocity increases as the frequency increases. On loaded trunk cable circuits, the velocity of high frequency components is less than that of the middle frequencies which are most prominent in ordinary telephone speech. Hence frequencies in the middle of the range arrive first and the higher frequencies arrive somewhat later. This difference is inappreciable on shorter circuits but for longer ones it may become great enough to be appreciable. The listener hears as the effect of this difference a sort of " chirping sounds " which reduce the intelligibility of speech to an appreciable extent and cause a certain amount of annoyance to the speakers.

This effect can, however, be corrected by installing at repeater stations along the circuit of " phase-compensating networks " which no doubt equalises the delays for various frequencies but introduces additional delay.

(b) The second effect of low velocity of transmission over telephone circuits is to be found in the " transmission time itself." In the ordinary case the time elapsed between the speaking of a word at one end of a circuit and its reproduction at the distant end is inappreciable, but for very long circuits this also requires consideration. If too great a time is required for onward transmission of speech and for return transmission of reply, the vocal interchange of ideas is interfered with. This consideration has led to the conclusion that the total transmission time over any telephone circuit should not in any case exceed $\frac{1}{4}$ of a second (250 milli-seconds). From this it is evident that the velocity of transmission of 20,000 miles/sec. (which is the usual figure for international loaded trunk cable circuits in service) would not be adequate in near future for connections between widely separated parts of the earth. The use of high frequency carrier currents for operation over unloaded open-wire or cable circuits thus affords great advantages in this respect over voice-frequency working on loaded cable circuits.

(c) The third effect of the low velocity of transmission is the annoyance caused by the " echoes " which may arise due to imperfection of line balances at the terminal repeaters of a four-wire loaded trunk cable circuit. On a thousand miles of such a circuit with a transmission velocity of 10,000 miles/sec. (say), the speaker may hear in his receiver the echoes of his own words 0·2, 0·4, 0·6 .... seconds after he has spoken and the listener at the other end may hear not only the direct transmission but echoes delayed by 0·2 of a second. Such effects seriously interfere with conversation, the amount of interference increasing with the amount of delay. The effect of echoes can be reduced by increasing the velocity

of transmission over the circuit, by reducing the amount of echo current and by providing the circuit with "voice-operated echo-suppressors" installed at the centre of the system.

The study of transmission time for transmission over telephone circuits of different types and its effects have already engaged the attention of a few workers. But little has been done to study the transmission times in case of various telephone apparatus and networks (used in terminal and repeater stations), and their variation with various frequency components of the speech. As far as author's information goes, there is only one paper by C. E. Lane entitled[*] "Phase distortion in telephone apparatus" on the subject and this also has not taken into consideration all typical apparatus and network. The importance of this study is specially enhanced by rapid growth of multiplex communication systems (for instance, simultaneous operation of voice-frequency and carrier frequency telephone channels on the same circuit), since in such cases frequency band of each channel has to pass through several additional net-works and is thus liable to suffer additional delay. The present paper relates to measurement of delay for transmission of alternating currents of various frequencies through some common telephone networks and apparatus, for instance, wave-filters, telephone transformers, telephone repeating coils and audio-frequency amplifier undertaken by the author.

2. THEORY OF THE METHOD OF MEASUREMENT OF PHASE-SHIFT.

For obtaining the delays at various frequencies it is necessary to measure the phase-shifts suffered by various frequency components on transmission through various apparatus and network.
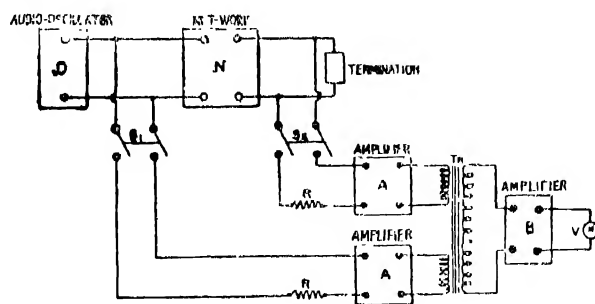
FIGURE 1.

Circuit for measuring phase-shift

The method employed in the measurement of phase-shift is similar to that employed by Messrs Hinton, Rendall and White in their paper on "Phase relations in unbalanced two-way telephone repeaters." [†] The schematic diagram of the measuring circuit is shown in figure 1.

* Bell System Technical Journal, Vol. IX, July, 1930, pp 493, 521.
† Electrical Communication, Vol. VIII, July, 1929.

Suppose a wave of angular frequency ω, whose instantaneous value of potential is denoted by E_1, is impressed at the input of the network (Fig. 1) under consideration, and let E_2 be its instantaneous value at its output. Then if β denotes the amount of phase-shift in radians and $20 \log_{10} m$ the attenuation in decibels suffered by the wave in passing through the network, the two potentials may be represented by

$$E_1 = m E_0 \sin \omega t, \qquad \text{(at the input)} \qquad \ldots \qquad \ldots \quad (3)$$

$$E_2 = E_0 \sin (\omega t \pm \beta), \qquad \text{(at the output)} \qquad \ldots \qquad \ldots \quad (4)$$

Therefore, $\qquad \dfrac{E_1}{E_2} = \dfrac{m \sin \omega t}{\sin (\omega t \pm \beta)} \qquad \ldots \qquad \ldots \quad (5)$

Now let the R. M. S. value of the voltage at the output of the amplifier B due to (3) be V_1 and that due to (4) be V_2. Also let V_{12} be the R. M. S. value when both (3) and (4) are applied simultaneously. Then, since the identical amplifiers A have been omitted in the present experiments and the amplifier B produces the same change in phase negligibly small in both the voltages we have,

$$V_1 = \frac{n m E_0}{\sqrt{2}} \qquad \ldots \qquad \ldots \quad (6)$$

$$V_2 = \frac{n E_0}{\sqrt{2}} \qquad \ldots \qquad \ldots \quad (7)$$

where n = voltage amplification given by amplifier B.

So that, $\qquad \dfrac{V_1}{V_2} = m \qquad \ldots \qquad \ldots \quad (8)$

On applying the two potentials together, the R.M.S. value V_{12} at the output of the amplifier B will be given by

$$V_{12} = \sqrt{\frac{E_0^2 n^2}{2\pi} \int_0^{2\pi} [\sin (\omega t \pm \beta) + m \sin \omega t]^2 \, d(\omega t)}$$

$$= \sqrt{\frac{E_0^2 n^2}{2\pi} \int_0^{2\pi} [(m + \cos \beta) \sin \omega t \pm \sin \beta . \cos \omega t]^2 \, d(\omega t)}$$

$$= \frac{m \, n \, E_0}{\sqrt{2}} . \sqrt{1 + \frac{2}{m} \cos \beta + \frac{1}{m^2}} \qquad \ldots \quad (9)$$

Hence, $\qquad \left(\dfrac{V_{12}}{V_1}\right)^2 = 1 + \dfrac{2}{m} \cos \beta + \dfrac{1}{m^2}$

$$\therefore \quad \beta = \cos^{-1}\left[\frac{m}{2}\left\{\left(\frac{V_{12}}{V_1}\right)^2 - 1 - \frac{1}{m^2}\right\}\right] \qquad \ldots \quad (10)$$

3. MEASUREMENT.

For measurement, an audio-frequency oscillator ' o ' of range from 20 — 10,000 c.p.s. (Type 74300-c) manufactured by the Standard Telephones and Cables Coy. Ltd., has been used. ' N ' is the four-terminal network or apparatus under test. S_1 and S_2 are two switches placed in the parallel leads at the input and the output of the network respectively. T_a is a special type of transformer having two similar winding on the primary side, the ratio of transformation being 1:2. The voltage amplifier B is of the ordinary resistance-capacitance coupling type while the measuring instrument is a valve-voltmeter, constructed and calibrated by the author in the laboratory. Two equal high resistances R were inserted in the parallel circuits taken from input and output sides of the network to increase the impedances of those circuits. The oscillator was first of all adjusted for a certain frequency. The switches were then closed first separately and then together and the corresponding deflections in the milli-ammeter of the valve-voltmeter were observed. Corresponding values V_1, V_2, V_{12} were then found out from the calibration curve of the voltmeter. Subsequently the phase-shift was calculated from equations (9) and (10) of the previous section. This procedure was repeated for several frequencies and corresponding phase-shifts obtained. Phase-shift measurements were carried out in case of wave-filters, transformers, repeating coils and audio-amplifier.

From phase-shift-frequency characteristic, the value of $\left(\dfrac{d\beta}{dw}\right)$ which is the measure of delay was calculated in milli-seconds. Graphs showing the variation of phase-shift and delay with frequency were then plotted on the same sheet as shown in figures 3, 5, 7, 8a, 8b, 10 and 12.
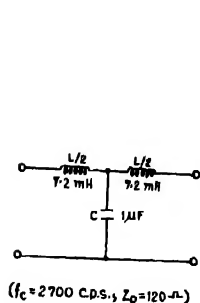
FIGURE 2.

FIGURE 3.

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P. B. Ghosh
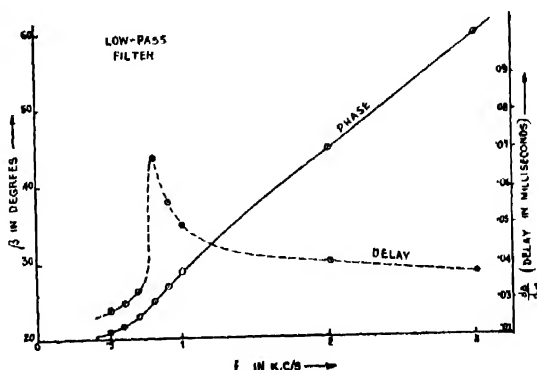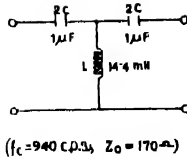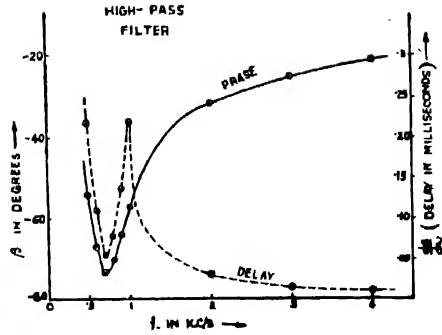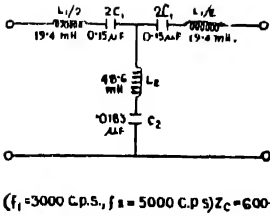
FIGURE 4.
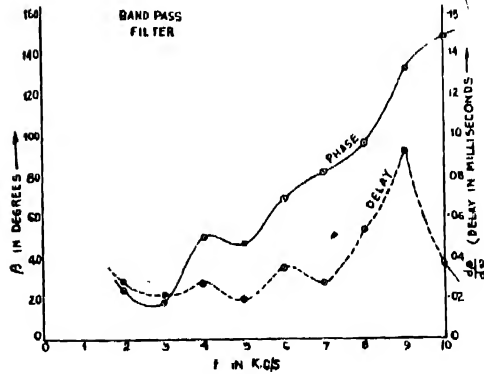
FIGURE 5.

FIGURE 6.

FIGURE 7.

4. DISCUSSION OF RESULTS.

(a) *Wave-filters.*

1. Low-pass filter section:—

A symmetrical, ' T ' type, low-pass filter section of cut-off frequency, $f_c = 2700$ c.p.s. and characteristic impedance $z_0 = 120\Omega$, as shown in figure 2, was taken. Phase and delay characteristics are shown in figure 3. The magnitude of the delay varied from ·066 to ·028 milli-seconds in the range 0·6–3·0 k.c/s. and was constant in the range 1·0 − 3·0 k.c/s.

2. High-pass filter section:—

A symmetrical, ' T ' type, high-pass filter section of cut-off frequency, f_c = 1000 c.p.s. and characteristic impedance z_0 = 170Ω, as shown in figure 4 was taken. Phase and delay characteristics are shown in figure 5. Within the transmission band, the delay decreased from about 0·22 milli-seconds near the cut-off frequency to very small values at higher frequencies but outside the band the variation was irregular.

3. Band-pass filter section:—

A m-derived, four element, T structure in which lower cut-off frequency f_1 = 3000 c.p.s.; higher cut-off frequency f_2 = 5000 c.p.s. frequency of infinite attenuation f_∞ = 5500 c.p.s. and characteristic impedance z_0 = 600 as shown in figure 6 was taken. Phase and delay characteristics are shown in figure 7. Within the transmission band, the delay was fairly constant at ·02 milli-seconds but outside the band it varied irregularly.

(b) *Transformers.*

Two types of transformers—Intervalve and Output—have been studied. A Ferranti Intervalve Transformer (Type AF6, Ratio 1:7) and a Ferranti Output Transformer (Type CPMS, Ratio 1:1) were taken. Phase and delay characteristics are shown in figures 8(a) and 8 (b). In case of the intervalve transformer, the delay was constant between 1·5 − 5·5 k.c/s and varied below 1·5 k.c/s. In case of the output transformer, the variation of delay is irregular and is from ·02 to ·028 milli-seconds.

Fig. 8A.

Fig. 8B.
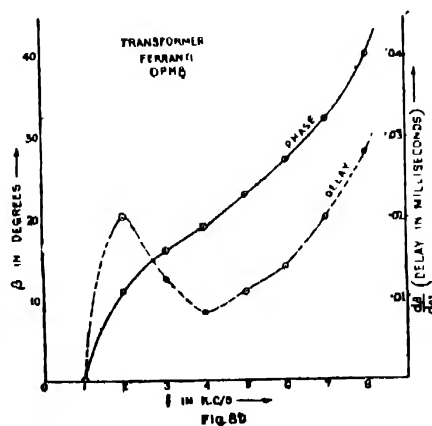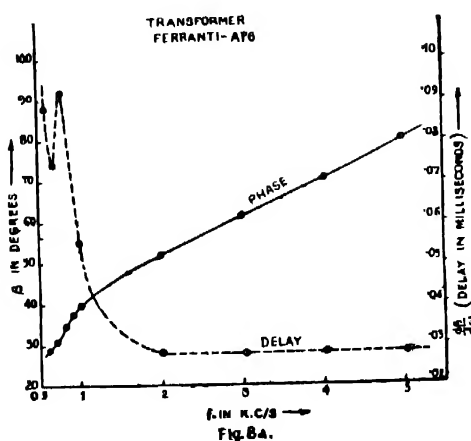
(c)   *Repeating Coil.*

A telephone repeating coil (No. C 4153-1, ratio of transformation 1:1) manufactured by the Standard Telephone and Cables Coy. Ltd., was taken. Phase and delay characteristics are shown in figure 10. In this case the delay is practically negligible.
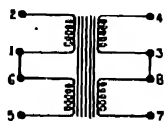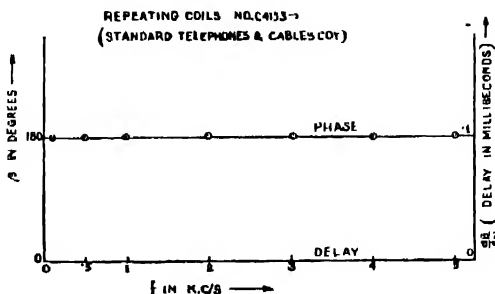
FIGURE 9.   FIGURE 10.

(d)   *Audio-Amplifier.*

A two-stage amplifier as shown in figure 11 was taken. Phase and delay characteristics are shown in figure 12. In this case the delay decreases from ·046 milli-seconds at 0·5 k.c/s. to about ·01 ' milli-seconds at 7 k.c/s.
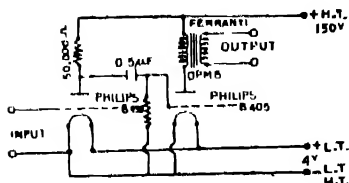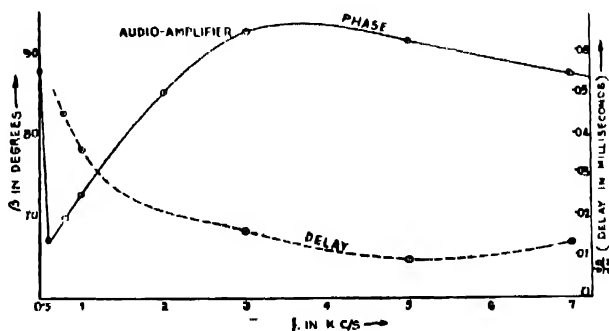
FIGURE 11.   FIGURE 12.

Delays of other frequency components with respect to the mean or mid-frequency component in the above cases are shown in table I.

TABLE I.

Apparatus or Network	Delays with reference to mean or mid-frequency in milli-seconds.				
	500	1000	3000	4000	5000
Wave-Filters					
Low-pass	+ ·022 m.s.	0	+ ·015 m.s.		
Band-pass			+ ·006 m.s.	0 m.s.	+ ·008 m.s.
Transformers					
Intervalve	−0·045 m s.	0 m.s.	+ ·027 m.s.		+ ·027 m.s.
Output	0 m.s.	0 m.s.	−0·0125 m.s.		−0·011 m.s.
Repeating coil	0 m.s	0 m.s.	0 m.s.		0 m.s.
Audio-Amplifier	− ·029 m.s.	0 m s.	+ ·020 m.s.		+ ·027 m.s.

Experiment shows that when individual apparatus or network is considered, the order of the delay is so small as to cause no annoyance and the variation of delay with frequency is such as to cause no appreciable phase-distortion. In actual case, where several filters (each consisting of two to three sections), transformers, amplifiers, etc. are connected to the line circuit, the total delay will be large, more especially if the line circuit is long.

5. ACKNOWLEDGMENTS.

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3 Harry Nyquist, Smart Brand,—*Bell System Tech. Jour.*, **9**, 522, (1930).

4 Steinberg, J. C., *Bell System Tech. Jour.*, **9**, 550, (1930).

ON THE POLARISATION OF RAMAN LINES OF SOME ORGANIC COMPOUNDS.

By BINOY KANTA CHAUDHURI, M.Sc.

Plate V

ABSTRACT. The polarisation of the Raman lines of piperidine, ethylene diamine, diethylamine and triethylamine has been experimentally investigated and the symmetry of the first two of these molecules has been discussed. It is shown that the piperidine molecule has a puckered structure having the symmetry C_{1h} and that probably there is no free rotation about the C—C axis in the molecule of ethylene diamine, though there is such a rotation of each of the NH_2 groups about the C—N bonds.

INTRODUCTION.

It is well known that the number of Raman lines which can be observed in the case of any substance depends not only on the number of atoms on the molecule but also on the symmetry possessed by the molecule. It is not possible, however, to determine the symmetry of the molecule from a knowledge of the number of Raman lines alone but besides this, a knowledge of the state of polarisation of the Raman lines also becomes necessary. In the present investigation the polarisation of Raman lines of piperidine, ethylene diamine, diethylamine, and triethylamine has been studied experimentally and an attempt has been made to arrive at a conclusion regarding the structure of the piperidine and ethylene diamine molecules.

EXPERIMENTAL.

The liquids investigated were all of pure quality and they were distilled in vacuum before being used. The amines were kept in air-tight tubes during exposure because they fumed copiously when brought in contact with atmospheric moisture. The liquids were illuminated by condensing light from a mercury arc on the tubes containing them with the help of a powerful condenser. The double image prism used by Gupta [1] was used in the present investigation in order to photograph the two components of the scattered spectrum simultaneously. As has been mentioned by Gupta, the planes of vibration of the light vector in one of the components is inclined to the vertical at an angle of about 48° when separation of the two components is in the vertical direction. For this reason the axis of the incident beam focussed on the tube was so adjusted by making the axis of the condenser properly inclined to the vertical and placing

the tube and the mercury arc on its axis that the axis of the incident beam was at right angles to the light vector of one of the components of the scattered radiation passing through the double image prism and coincident with the other. Though the adjustment is a little difficult, this peculiar property of the double image prism has one advantage, viz., the two components being inclined to the vertical at an angle very near to $45°$, there is appreciably no loss of intensity of any of the components due to reflection at the surfaces of the prisms inside the spectrograph. With the same arrangement the state of polarisation of Raman lines of carbon tetrachloride was studied and it was observed that the observed values reduced to values observed under ideal conditions by Cabannes and Rousset and also by other authors when o'1 was subtracted from each of these values of ρ, the depolarisation factor. This correction was applied to the results obtained in other cases.

Intensity marks were obtained by the method of variation of width of the slit of the spectrograph used and a standardised tungsten ribbon lamp was used as a source of light for this purpose. The microphotometric records of the spectrograms as well as of intensity marks were obtained with the help of a Moll's microphotometer. Some of the spectrograms contained a little background. In order to correct for this, the total density at the centre of one of the components of any Raman line was first determined and then that of the background was also determined from the microphotometric records. The corresponding intensities were then obtained from the blackening-log intensity curve for the corresponding wave-length and subtracting one from the other, the relative intensity of this component of the Raman line was determined. Similar procedure was adopted to determine the intensity on the same scale of the other component and by dividing the weak component by the strong one, the uncorrected value of ρ was obtained. From this the correction term mentioned above was subtracted and the corrected value of ρ for natural incident light was obtained. The spectrograms have been reproduced in Plate V in order to show how with the arrangement mentioned above, almost the actual state of polarisation is observed on the spectrograms, the loss of the stronger component being very small with this arrangement. It can be seen as for instance, that the line 1442 cm^{-1} due to the deformation oscillation of CH_2 group is almost completely depolarised and when the small correction term is applied, the value reduces to the ideal one, $6/7$. The small correction is necessary probably because there was want of transversality of the incident beam.

In some cases where there were overlapping of different Raman lines on one another, a filter of *m*-dinitrobenzene in benzene was used. In the case of piperidine two spectrograms were obtained, one without any filter and the other with a filter of iodine dissolved in carbon tetrachloride. The latter picture showed clearly the state of polarisation of the hydrogen lines having $\Delta\nu$ values greater than 2500 cm^{-1}. The results obtained are tabulated in tables I-IV.
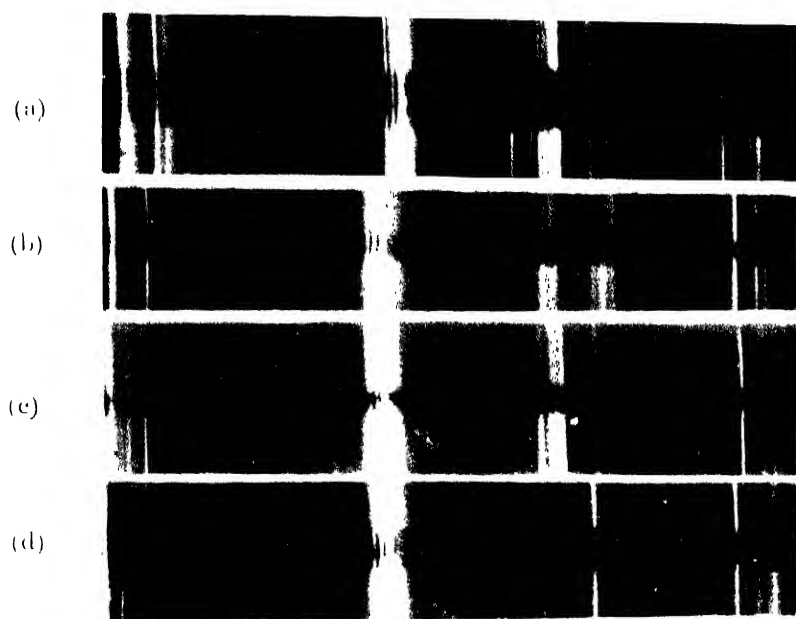
Polarisation of Raman lines

(a) Piperidine

(b) Ethylenediamine

(c) Diethylamine

(d) Triethylamine

TABLE I.

Piperidine $C_6H_{11}N$.

No of Raman lines.	$\Delta\nu$ in cm^{-1} of Raman lines.	Intensity.	Depolarisation factor	No of Raman lines.	$\Delta\nu$ in cm^{-1} of Raman lines.	Intensity	Depolarisation factor
1	243	0	dp	12	1287	2	·54
2	400	1	p	13	1342	0	dp
3	443	1	dp	14	1442	3b	·88
4	755	0b	7 5	15	2655	1	p
5	817	8	·37	16	2730	2	·24
6	857	0	p	17	2803	··	·22
7	1006	1	p	18	2852	4	·25
8	1035	·	·38	19	2892	2	·36
9	1049	2	·89	20	2931	8b	·34
10	1146	2	·9	21	3307	0	p
11	1265	2	·85	22	3339	1b	p

TABLE II.

Ethylene diamine $C_2H_8N_2$

No. of Raman lines.	$\Delta\nu$ in cm^{-1} of Raman lines.	I	ρ
1	469	1	·27
2	833	2	·65
3	982	1	·46
4	1100	·	·3
5	1301	1	·82
6	1352	1	·0
7	1443	2	87
8	2581	4 br	·51
9	2917	2 br	·72
10	3292	8 br	·24
11	3360	4	·68

TABLE III.

Diethylamine $C_4H_{11}N$

No. of Raman lines.	$\Delta\nu$ in cm^{-1} of Raman lines.	I	ρ
1	427	4	·25
2	871	2 br	·32
3	1447	8 br	·0
4	2851	8 br	·44
5	2872	6 br	·63
6	2925	10	·22
7	2970	8	·84
8	3315	4 br	·25

6

| TABLE IV. |
| Triethylamine $C_6H_{15}N$ |

No. of Raman lines.	$\Delta \nu$ in cm^{-1} of Raman lines.	I	ρ
1	435	2	·5
2	736	4	·3
3	915	4 br	·9
4	997	1	·68
5	1069	6	·9
6	1286	1	·72
7	1433	8	·86
8	2874	4	·4
9	2932	8 br	·3
10	2966	4	·8

| TABLE V. |
| Carbon tetrachloride CCl_4 |

No. of Raman lines.	$\Delta \nu$ in cm^{-1} of Raman lines.	I	ρ
1	217	8	·86
2	313	8	·78
3	459	10	·05
4	763	6	·86
5	792	6	·86

DISCUSION OF RESULTS.

Piperidine—The symmetry of the piperidine molecule has been discussed recently by Kohlrausch and Stockmair [2] but no definite conclusion could be drawn by them regarding the symmetry of the molecule because the data for polarisation of the Raman lines were not available. The molecule may have either a plane or puckered structure. In the case of the plane structure the symmetry would be C_{2v}, the twofold axis of rotation passing through the nitrogen atom and the diametrically opposite carbon atom and one of the two planes of reflection passing through this axis lies in the plane of the molecule, the other being perpendicular to the plane as shown in figure 1 (a). In the case of the puckered structure, it may have again two forms, both having the same symmetry C_{1h}, one being called "Sessel" and the other "Wannen" form as shown in figures 1 (b) and 1 (c) respectively. The latter two forms cannot be distinguished from each other from a study of the polarisation of the Raman lines but it can be decided whether the molecule has a plane structure or a puckered one.

(a)   (b)   (c)
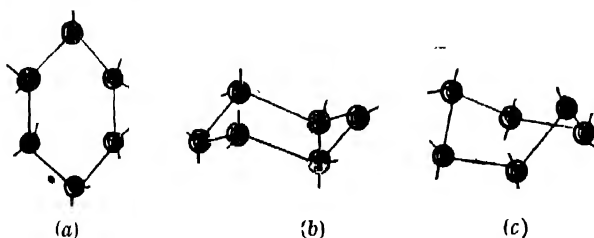
FIGURE 1.

As there are altogether 17 atoms in the piperidine molecule, the maximum number of lines in the Raman spectrum may be $51-6=45$ in the case of the plane as well as the puckered structure. The forms of vibration of the ring as well as of the CH_2 group of the cyclohexane molecule have been shown diagramatically by Kohlrausch and Stockmair in the paper mentioned above. These forms of vibration of the closed ring of the piperidine molecule as well as those of the CH_2 group are reproduced in figure 2. In a more recent paper Kahovec and Kohlrausch [3] have deduced the number of possible polarised and depolarised lines which would
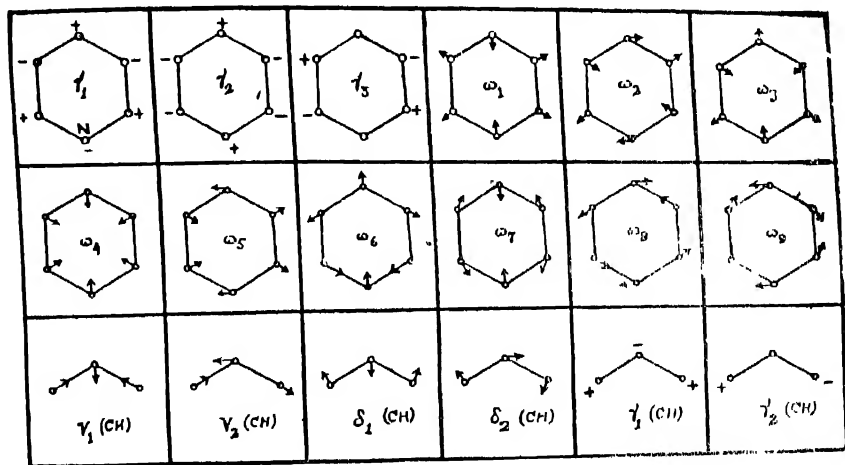
FIGURE 2.

be expected in the case of the piperidine molecule if it would have the symmetry C_{1h} ($=C_s$), *i.e.*, if the molecule would have a puckered structure. These lines are listed in table V, the lines due to $N-H$ group not being included in the table. The letters "s" and "as" denote symmetric and anti-symmetric to the plane; similarly "p" and "dp" denote respectively polarised and depolarised.

TABLE V.

σ y		Piperidine—C_{1h}	
s	p	γ_1 γ_2 ω_1 ω_3 ω_4 ω_6 ω_7	$3\gamma_1$ $2\gamma_2$ $3\delta_1$ $2\delta_2$ $3\nu_1$ $2\nu_2$
as	dp	γ_2 ω_2 ω_5 ω_8 ω_9	$2\gamma_1$ $3\gamma_2$ $2\delta_1$ $3\delta_2$ $2\nu_1$ $3\nu_3$
		Vibrations of the ring	CH vibrations

The different CH vibrations arise from the different phase relations among these vibrations of the individual CH_2 groups present in the whole molecule. As for instance, the movement of the carbon atom in the case of δ_1 and ν_1 oscillations of the CH_2 groups is of identical nature and also only those vibrations of the ring in which similar movements of the carbon atoms take place can give rise to δ, and ν, (CH) oscillations; hence there are as many δ_1 (CH) oscillations as there are ν_1 (CH) oscillations. Similarly there are as many δ_2 (CH) oscillations as there are ν_2 (CH) oscillations. It can be seen from table V that there should be 5 polarised Raman lines (3 ν_1 and 2 ν_2) having $\triangle \nu$ greater than 2500 cm^{-1} if the symmetry of the molecule be C_{1h}. If, however, the molecule would have a planar structure, the symmetry would be C_{2v} and the two (CH) vibrations 2 ν_2 which are symmetric to the plane of symmetry would be antisymmetric to the twofold axis of rotation passing through the nitrogen atom and the carbon atom opposite to it, and in that case these lines would be depolarised. Hence for the planar structure there can be only 3 (CH) oscillations of frequencies greater than 2500 cm^{-1} which are polarised. Actually, however, there are six such polarised lines, as can be seen from table I. It can therefore be definitely concluded that the structure of the piperidine molecule is a puckered one. Probably one of these six lines is not due to any fundamental oscillation.

In an attempt to identify the frequencies of oscillations of the ring, Kahovec and Kohlrausch have pointed out that in the case of piperidine; $\omega_4 = 807$ cm^{-1}, This line is intense and is observed to be well polarised by the present author, and therefore the above assignment seems to be quite correct. The authors mentioned above have not arrived at any definite conclusion regarding the other frequencies. An attempt may be made here to identify the other frequencies also, after the state of polarisation of the lines is known. In the case of the cyclohexane molecule, each of the pairs of oscillations, $\omega_{1,2}$, $\omega_{5,6}$ and $\omega_{7,8}$ gives a twofold degenerate line which is depolarised. When one of the carbon atoms is replaced by a nitrogen atom as in the piperidine molecule, the degeneracy is removed and three pairs of lines are expected to be produced by these six modes of vibration. As can be seen from figure 2, of these vibrations ω_1, ω_6 and ω_7 ought to give polarised Raman lines and ω_2, ω_5 and ω_8 depolarised Raman lines. As has been pointed out by Kahovec and Kohlrausch, $\omega_{1,2}$ in the case of cyclohexane can be identified with the line 425 cm^{-1}, though the actual calculation, taking ω_1 equal to 809 cm^{-1} gives $\omega_{1,2} = 520$ cm^{-1}. In the case of piperidine the lines in this region are 400 cm^{-1} and 443 cm^{-1}; the former being polarised and the latter depolarised, they can respectively represent ω_1 and ω_2. Similar arguments lead to the conclusion that probably the lines 1035 cm^{-1}, 1049 cm^{-1}, 1265 cm^{-1} and 1287 cm^{-1} represent ω_6, ω_5, ω_8 and ω_7 respectively. Kahovec and Kohlrausch have suggested that ω_3 lies in the region 755 cm^{-1}. This line, however, does not seem to be well polarised; on the other hand, the line 857 (o) is well polarised and may be identified with ω_3.

The existence of the line 1006 cm^{-1} in the case of piperidine is confirmed by the present investigation. There is also a polarised line at 3307 cm^{-1} which is feeble and was observed by Sirkar[4] previously but the presence of this line is not expected from theoretical point of view. Probably, piperidine being highly hygroscopic, a small percentage of molecules being acted upon by moisture gives rise to this line.

Ethylene diamine.

It can be seen from table II that of the two lines 3292 cm^{-1} and 3360 cm^{-1} due to the N-H vibration of the NH$_2$ group the former is well polarised and the latter completely depolarised. Since there are two NH$_2$ groups in the molecule a knowlege of their relative orientations in the molecule is necessary in order to ascertain which types of vibrations are responsible for these two lines. The structure of the molecule has been discussed by Zahn[5] who has concluded from the results of measurement of the permanent electric moment of the molecule that the observed value of μ agrees with the value calculated with the assumption that either (1) there is free rotation about the two C−C bonds and about C−N bonds, or (2) there is free rotation of the two NH$_2$ groups in the transposition about the C−C bonds. It can be easily seen that if the two NH$_2$ groups were fixed in the trans position the molecule would possess a centre of symmetry and a plane of reflection and the symmetric vibration of the two NH$_2$ groups in phase ν_1, (π, s) would be intense and well polarised in the Raman effect but in that case the value of μ would be zero. Hence the free rotation of the NH$_2$ groups has to be taken into consideration. In the case (2) of such a free rotation of the NH$_2$ groups about the C−N bond, the centre of symmetry as well as the plane of reflection are absent for most of the time in one complete rotation and therefore the two groups vibrate independent of each other, there being absolutely no phase relation between the vibrations of the two NH$_2$ groups, so that the polarisation character of these Raman lines depend on the character of the oscillations of the single group and thus the symmetric vibration gives the line 3292 cm^{-1} and the completely depolarised line 3360 cm^{-1} ($\rho = \frac{6}{7}$) is due to antisymmetric vibration of each group. At the time of such vibration, the CN bond also undergoes a little deformation but that does not affect very much the frequency of the vibration of the NH$_2$ groups, because even in the case of the ethylene molecule the vibration ν_1 (π, s) which entails an expansion and contraction of the C=C bond, the frequency is 3719 cm^{-1}, i.e., only slightly higher than the normal value of the vibration of the comparatively free CH$_2$ group. Kohlrausch[6] has calculated the angle α between NH bonds and in the NH$_2$ group by assuming the mean value of ν (π) ν (σ) and δ (π) to be 3313 cm^{-1}, 3367 cm^{-1} and 1113 cm^{-1} respectively. In the present case an attempt may be made

to find the value of f and α by assuming a valence force system and with
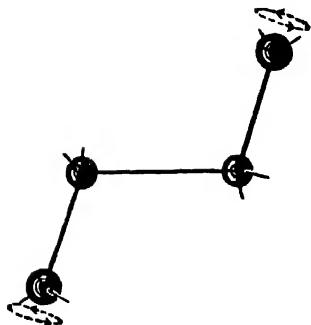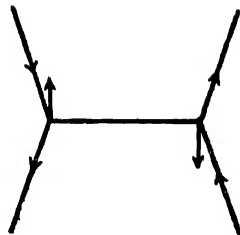
<div style="text-align:center">FIGURE 3.   FIGURE 4.</div>

the help of the simplified formulae,

$$\nu\,(\pi)=\frac{f}{m}\left[\,1-(1-p)\cos^2\frac{\alpha}{2}\,\right]$$

and

$$\nu\,(\sigma)=\frac{f}{m}\left[\,p+(1-p)\cos^2\frac{\alpha}{2}\,\right],$$

the values of f and α are found to be $6\cdot053\times10^5$ dynes/cm. and $107^\circ\,48'$ respectively. As regards the polarisation characters of the two lines 2851 cm^{-1} and 2917 cm^{-1}, it can be definitely stated that both of these two lines are partially polarised and none of them is completely depolarised. If it is assumed that the two CH$_2$ groups are so arranged in the molecule that there is a centre of symmetry when only these two groups are taken into consideration, as shown in figure 3 the vibration antisymmetric to the centre of symmetry will be forbidden and only those symmetric to the centre of symmetry will be observed in Raman effect. The symmetric C$-$H valence oscillation of the two groups in phase with each other will be most intense and polarised and probably the line 2851 cm^{-1} can be identified with this vibration ; the other line 2917 cm^{-1} is probably due to the vibration shown in figure 4 in which the centre of symmetry is retained. If this view be correct, it can be concluded that there is no free rotation round the C$-$C axis in this particular molecule. Since there is no doubt regarding the free rotation of the NH$_2$ group and as due to such a rotation the antisymmetric vibration of the NH$_2$ group is completely depolarised, it might be expected that if the rotation about C$-$C axis were present, one of the Raman lines due to C$-$H valence oscillation would be completely depolarised. Since actually it is not so, the above conclusion, that probably there is no rotation about the C$-$C

axis is drawn. The angle between two $C-H$ bonds in a CH_2 group calculated by applying the valence force system is about $105° 36'$ which shows that actually the angle may be about the tetrahedral angle.

In conclusion, the author desires to express his grateful thanks to Prof. D. M. Bose for his kind interest in the work and for providing the author with all the facilities for doing the work. The work was carried on under the suggestion and helpful guidance of Dr. S. C. Sirkar to whom also the author's best thanks are due.

PALIT LABORATOY OF PHYSICS :
92, UPPER CIRCULAR ROAD,
        CALCUTTA.

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ON THE HYPER-FINE STRUCTURE OF THE λ 4336·89, $sp^{33}D_2 - 5p^BD_1$ LINE IN THE FIRST SPARK SPECTRUM OF ARSENIC AND ITS NUCLEAR SPIN

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Plate VI.

ABSTRACT. The hyper-fine structure of the $\lambda4336\cdot89$, $sp^{33}D_2-5p^3D_1$ line in the first spark spectrum of arsenic has been studied and it is found that this line is a perfectly resolved, sharp, regular quartet degraded to the violet. The components are at intervals of 159, 115 and 67. It is found that this line follows the interval and intensity rules with remarkable accuracy. The analysis definitely shows that the nuclear spin of arsenic is 3/2 as previously proposed by S. Tolansky.

INTRODUCTION.

No investigation has so far been made on the hyper-fine structure of any of the lines of the first spark spectrum of arsenic in the ultra-violet region. While studying the structures of these lines, the details of which will be found elsewhere, the $\lambda4336\cdot89$, $sp^{33}D_2-5p^3D_1$ line at the ultra-violet border of the visible region was also photographed and studied. S. Tolansky[1] and A. S. Rao [2] have both examined this line. Rao gets only three components and Tolansky gets four as theoretically expected and observed here, but his last two components as admitted by him (*loc. cit.*) are not well resolved and as in his investigation he did not use a hollow-cathode discharge tube for exciting the lines so the structure of this line was again studied and investigated using a hollow-cathode discharge tube. Experience has shown that this is the only type of discharge tube which will enable the Doppler and Stark broadening effects to be sufficiently reduced so as to obtain reliable numerical values of the structures.

The gross-structure multiplet analysis of As II lines has been made by A. S. Rao [3] and his line classifications have been employed here.

EXPERIMENTAL.

It was found extremely difficult to excite the arsenic lines in a hollow-cathode discharge tube. Tolansky had also observed in his paper on As II

(*loc. cit.*) that it was extremely difficult to sputter arsenic in a hollow-cathode discharge tube and that neither he nor Badami who was working with antimony (which is very closely related to arsenic) succeeded in getting the lines strong enough for observational purposes. In the present investigation an iron hollow-cathode tube of the form designed by Paschen and modified by Schüler, about 7 cm. long and 1 cm. in internal diameter was used as the source. The tube was water-cooled and pure helium was circulated continuously through the tube at a pressure of about one millimetre. The current employed was varied from 100 to 300 milli-amperes at about one-thousand volts at the source. The arsenic lines obtained were however extremely faint and unsteady although hydrogen was almost completely suppressed by the red-hot copper-oxide used in the circuit. A second hollow-cathode tube with twice the internal diameter of the first tube was also constructed and tried. The voltage at the source was raised to about 2500 and the current was increased to 500 milli-amperes but there was not much improvement in the intensity of the lines until the purest arsenic free from all oxide was used. This was then heated in vacuum and made to deposit on the sides of the hollow cathode as a pure oxide-free coating of arsenic. A brilliant spectrum of As II was then observed. It was thus clear that neither the width of the hollow-cathode nor the complete suppression of hydrogen in the tube materially affects the sputtering action of arsenic or increases the brilliance of its lines. The principal condition is to obtain the arsenic as free from oxide as possible. This was obtained by deliberately omitting to heat the usual copper oxide furnace so that an appreciable amount of hydrogen was present in the discharge. The hydrogen in turn combines with the oxygen of the arsenic oxide coating finally reducing it to the pure metal which can easily be sputtered and which then gives a brilliant arsenic spectrum in the hollow-cathode discharge. The water-vapour formed is absorbed in liquid-air cooled chabazite traps. Chabazite, as an absorbent in place of the usual charcoal, has the advantage that it does not absorb helium in any large proportion, so that the helium supply to the discharge has not to be renewed too frequently. The fine structures of the lines were examined by means of two quartz Lummer plates of different thicknesses in conjunction with a Hilger E.2, spectrograph. Ilford hypersensitive Panchromatic plates, of speed 2500 and also Ilford Monarch plates, of speed 525 were used for this portion of the spectrum. Four to five hours of exposure were necessary to get good photographs in this region. The strongest component of the line investigated here is taken as the main or null line and the separations of the remainder are given, as usual, in units of $cm^{-1}. 10^{-3}$.

ANALYSIS.

Hyper-fine structures are of two distinct types, one of which is attributable to nuclear magnetism, and the other to nuclear mass, nuclear configuration or

electrical charge. The former arises when one and the same atom passes to different energy states and the latter from two or more distinct isotopic atoms. It is possible for both types of structure to occur together. But since arsenic does not have an isotope, the structure observed here is only of the magnetic type. To account for the multiplet structure the three quantum numbers L, S and J which define the orbital, spin and total angular momenta respectably, are fully employed and hence in order to account for the hyper-fine structure a fourth one is introduced. This is attributable to the nucleus, and with it is associated a magnetic moment. This magnetic moment gives rise to a mechanical moment, usually represented by $Ih/2\pi$ where I is termed the nuclear spin. The nuclear spin is capable of interacting with J. Hence the two vectors I and J combine vectorially to form a resultant quantum number, F, called the fine-structure quantum number, giving the total angular momentum of the whole atom. The values that F can have are then given by the vectorial relation $F = I + J$, so that the total number of combinations possible will be $2I + 1$, or $2J + 1$, according as J is larger or smaller than I. Hence the gross structure term divides into these fine structure levels. This then corresponds with the coupling of L and S to give a resultant J. But the energy of coupling between I and J is relatively much smaller and hence the resulting F sub-levels lie close together, and are then called the fine-structure sub-levels. The selection principle found to operate in the production of fine-structure, is that multiplet combinations will occur between those sub-levels for which F changes by ± 1 or 0 ($0 \longrightarrow 0$ being excluded.) The analysis of this line which results from the combination of two levels is given here.

Now, before this line can be analysed the structures of the lines $\lambda_{1190\cdot37}$, $5p^3D_1 - d$ and $\lambda_{3720\cdot31}$, $5p^3D_1 - f$ which have the $5p^3D_1$ term in common were very carefully examined. Both these lines were found to be single in all the plates examined. It is expected, therefore, that the structure in the term $5p^3D_1$ is either very small or negligible. Moreover, Tolansky has observed in his paper on arsenic (*loc. cit.*) that the line $\lambda_{5497\cdot98}$, $5s^3P_0 - 5p^3D_1$ is single. It has been explained before that the number of fine structure levels of a term is given by $2I + 1$ or $2J + 1$ (where I is the nuclear spin and J the total angular momentum) according as which has the smaller value. So, the term $5s^3P_0$ of this line remains single since the J value of this term is equal to zero ($2J + 1 = 2 \times 0 + 1 = 1$). Hence it follows that the structure in the term $5p^3D_1$ is very small and is not measurable. This then finally corroborates the conclusion that the $5p^3D_1$ term is single. This term, as will be seen, is present in the line $\lambda_{4336\cdot89}$ $sp^{33}D_2 - 5p^3D_1$, and this term being just shown to be single it follows that the quartet structure of this line is entirely due to and is the term structure of the term $sp^{33}D_2$. The observed intervals are 159, 115 and 67 and those calculated are 161, 115 and 69. The agreement is therefore remarkably good. The interval ratios obtained in this term are almost exactly as 7:5:3 as

demanded by a J value of 2 and nuclear spin of $3/2$. The analysis of this line then definitely proves that the nuclear spin of arsenic is $3/2$.

The photograph shown in figure 1, Plate VI clearly shows that this line is a perfectly resolved, sharp, regular quartet degraded to the violet. The term and the line structure are shown in figure 2.

$\lambda_4336\cdot89$, $sp^{33}D_2 - 5p^3D_1$. (As II.)
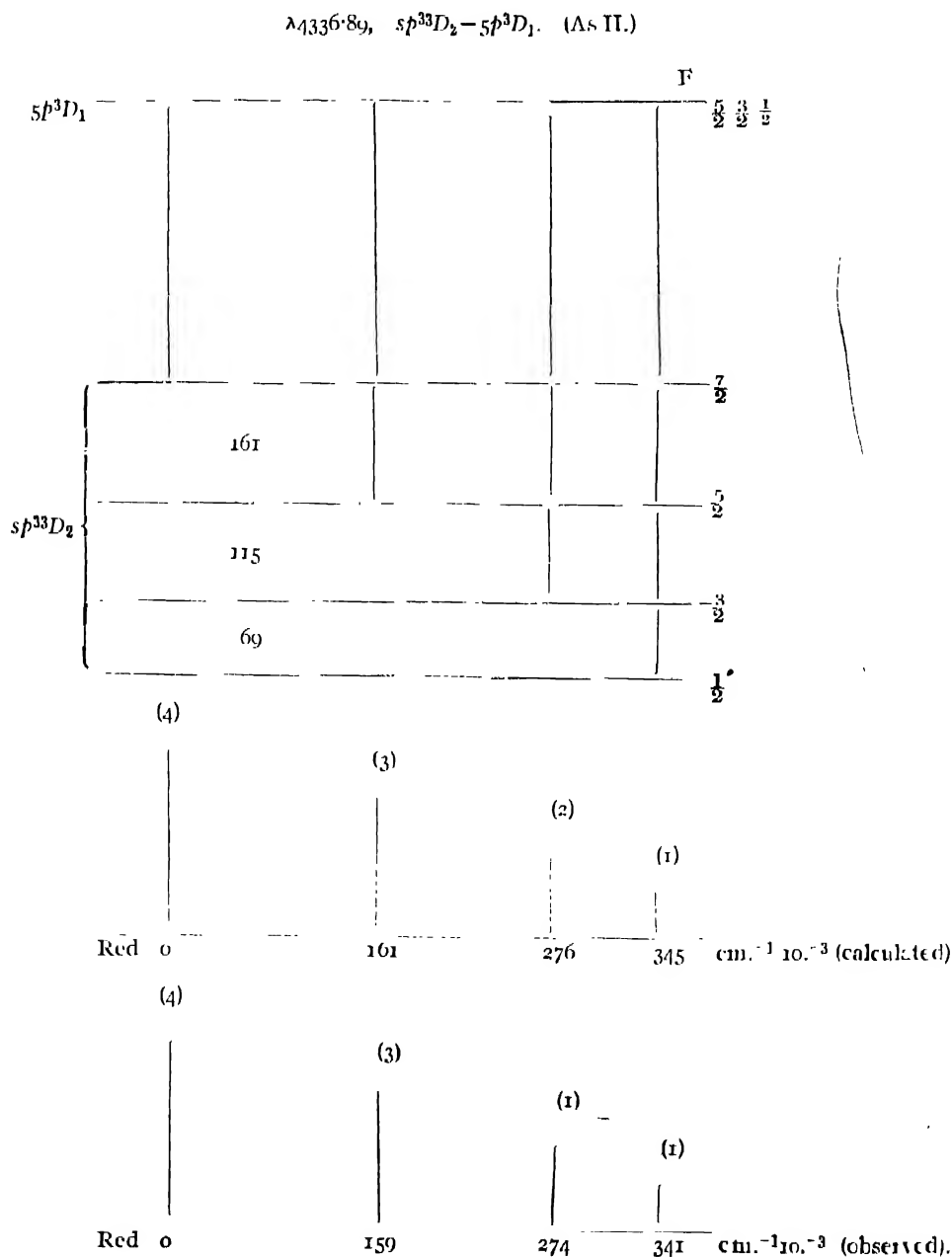
Figure 2.

Figure 1

Quartet Structure of λ 4336·89 $sp^5\ ^3D_2 - 5p^5D_1$
line in the first spark Spectrum of Arsenic
(Enlarged Photograph)

It may be remarked here that the examination of the structure of another As II line $\lambda 3948·74$, $sp^{33}D_2 - 5p^3P_1$ (found to be a sharp, well resolved, regular quartet degraded to the violet) in the ultra-violet region, the analysis of which will be found elsewhere, supports this investigation and indicates that the nuclear spin of arsenic should be $3/2$.

In conclusion the author wishes to thank Prof. O. W. Richardson, F.R.S., N.L., in whose laboratory at King's College, London, this investigation was carried on and Dr. W. E. Williams for all the help and facilities he gave him during the course of this work.

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X-RAY STUDIES ON ELECTRODEPOSITED CHROMIUM AND GOLD

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Plates VII and VIII.

ABSTRACT. Electrodeposited chromium and gold have been studied by the X-ray powder method, showing some correlation between current density and selective orientation and between hardness and breadth of diffracted lines. White lines, appearing as absorption ones, are reported in photograms of chromium. The origin of these is partially suggested. Gold deposits, electrolytically, obtained from baths, at different temperatures are found to yield diffraction lines, interspersed with spots, confirming thereby the axiom of Bancroft that lowering the temperature diminishes the size of crystal-grains. Intensity measurement has been made for lines of planes 111, 200, 220 311 and 222 of gold for different temper tures and size of grains has been calculated for chromium and gold at different current densities.

1. INTRODUCTION.

Clark with his co-workers and others [1] have made X-ray studies of electrodeposited metals in order to find out conditions controlling their brightness, hardness and other physical characteristics. X-ray examination has shown that electrodeposited metals have, generally, a crystalline structure and that the principal differences in the appearance and physical properties are caused by differences in the size or shape of the individual crystal grains. It would be clear, therefore, that such a study has a great importance in the industrial field.

W. D. Bancroft,[2] as far back as 1904, formulated certain axioms, regarding the structure of electrodeposited metals. One of these axioms may be stated here with advantage. This is

(1) Increasing the current density, increasing the potential difference at the cathode or lowering the temperature decreases the size of the crystals.

It should be emphasised that at best these principles, which are based on empirical data, are only a rough guide and it would be interesting to find out if modern investigations support or contradict these axioms.

Colour, lustre and wear resistance are some of the requisites which an electrodeposited material has to satisfy according to specific requirements and careful researches and extensive data are therefore required to settle factors, such as fineness of the grains or distortion of the crystal lattice or both which control the specific physical properties, the specimen has to exhibit.

In a recent paper, Basu and Hussain [3] have studied the variation in the degree of orientation of metal grains of silver with the variation of current densities and the breadth of diffraction lines with reference to the hardness of the surface of deposit and the size of metal grains. They also sought to find whether the same degree of crystalline orientation persists in all the crystalline planes.

With the same purpose as described in the earlier paragraph, as also with a view to test the truth of Bancroft's axiom quoted already, investigations have been undertaken by the present authors with chromium and gold, electrodeposited with different current densities. In the case of gold the effect of temperature variation of the bath on the deposit has also been studied.

2 CHROMIUM.

Levi and Tabet [1] have examined electrolytic chromium deposits by Scherrer's method. Photograms taken exhibit marked differences in the maxima of intensity and in width of lines for different preparations. The dimensions of particles have also been calculated. The detailed paper of Levi and Tabet is not available to the present authors, but from the abstract of the paper it appears that they worked with specimens obtained from different solutions, but not with specimens obtained with different current densities in the same solution as in our case. Moreover, the study of electrolytic chromium is desirable in view of important work of Bradley and Ollard [5] suggesting an allotropy of chromium in electrodeposition, with a characteristic new lattice.

3. PREPARATION OF SPECIMENS.

Specimens were obtained by depositing chromium on copper wires at different current densities, under exactly similar conditions with particular attention to the equality in the thickness of the deposits. Copper wires to be electroplated were first scratched with lime, then washed with alcohol and benzene, etched with dilute nitric acid (10 % solution) and finally washed with distilled water. Parts

Chromium

Gold

Gold
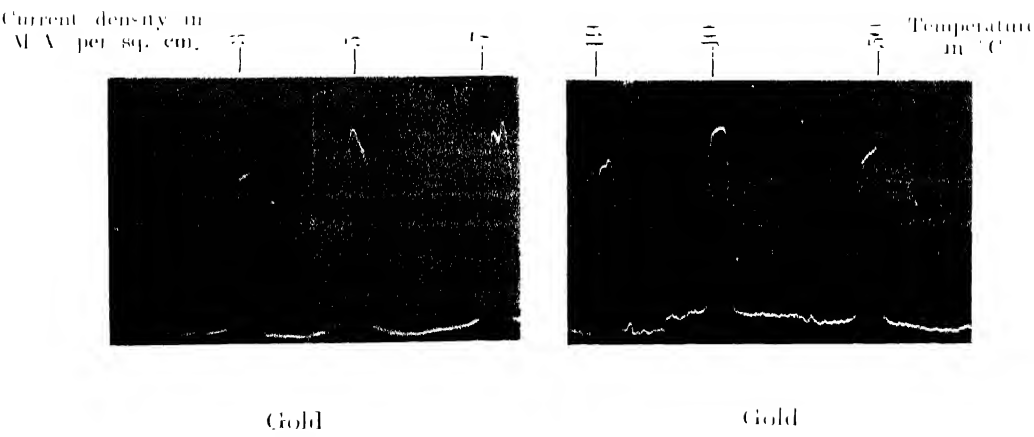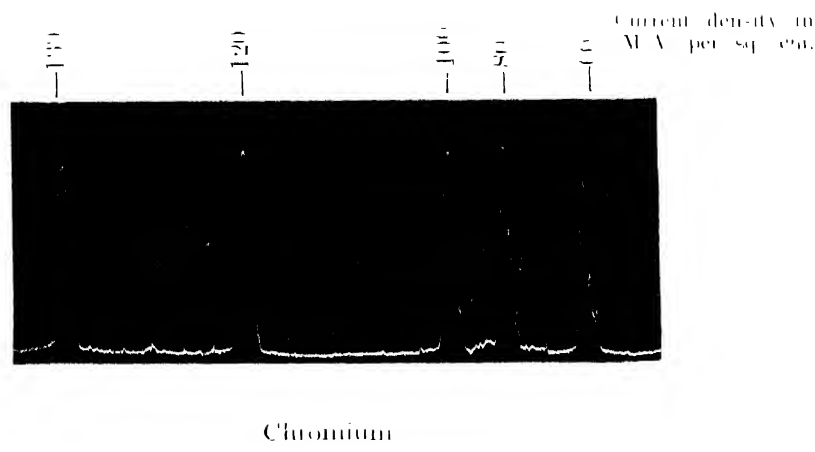
of the copper wire not to have the deposit were covered with a coating of melted paraffin wax and resin. The electroplating bath consisted of the following :—

Chromium Oxide pure (Merck) ...   125 gms.

Concentrated Sulphuric acid   ...   1·25 gms.

Distilled water   ...   500 c.c.

The solution was warmed and left overnight. The anodes were two plates of lead on either side of the cathode. A satisfactory-deposit was not obtainable with a current density below 60 m.A. and no deposit, at all, could be obtained with a current density below 50 m.A. Table I indicates the conditions of deposit on different specimens.

TABLE I.

Specimen.	Diameter of copper wire before deposit.	Current density in m.A./Sq.cm.	Time of deposit.	Diameter of specimen after deposit.	Temperature of the bath.	Relative brightness.	Degree of hardness.
1	0·81 m.m.	60	12 hrs	0·94 m.m.	30°C	100·00	100
2	,,	80	9 hrs	,,	,,	145·30	132
3	,,	100	6·5 ,.	,,	,,	140·30	168
4	,,	120	4·5 ,,	,,	,,	142·50	183
5	,,	130	3·5 ,,	,,	,,	122·00	208

4. ESTIMATION OF BRIGHTNESS.

In order to estimate the relative brightness, all the specimens were dipped in absolute alcohol for a thorough cleaning of the surface and were then photographed. Relative brightness was measured in the same way as was done with silver earlier. Microphotographs for different specimens are shown in figure 1, plate VII. The calculated values for relative brightness are given in the seventh column of table I. All values are computed taking the brightness for the 60 m.A. surface as 100.

The relative values of brightness given in table I as calculated from figure I show that they do not vary regularly with the increase in current density.

According to their appearance, chromium deposits fall into four classes, between which, however, there is no sharp dividing line. These are (a) milky, (b) bright, (c) frosty, (d) burnt in the order of increasing current density.[6] Frosty

and burnt deposits are usually an evidence of too high a current density for the prevailing temperature and the diminution of brightness with current density 130 m.A. may be due to this cause.

5. EXPERIMENTAL.

The powder method as developed by P. Debye and P. Scherrer[7] was adopted to obtain the diffraction spectra. For this purpose a freshly sealed Hadding tube with an aluminium window of 7μ thickness was taken. A copper anticathode and super speed selochrome films were used. The process of development was on the same line as with silver.[5]

Exposure was first given for all specimens, for 10 hours, the current and voltage of the tube being 10 m.A and 50 k. V. respectively. No diffraction line was obtainable with any of the specimens With an exposure of 20 hours, a single diffracted line (from face with indices 110) could be obtained and that also with specimens of 130, 120 and 100 m.amp. current densities only. Figure 2, plate VIII shows the intensity of diffracted lines with different specimens. (Black spots on lines of photograms in figure 2 and in figure 4 for current density 5 m.A. are due to ink marks, put for the convenience of measurement on the negative.) It will be observed that the intensity of the diffracted line for the specimen of 100 m A. current density, is very weak. The calculated intensities by microphotometer method were reduced in terms of the intensity of 110 line for the current density 100 m A. which was found to be minimum in our case and is expressed as 100. Relative values are given in table II.

6. BREADTH AND HARDNESS OF SPECTRAL LINES.

The breadth, as measured from microphotograms in the usual way was reduced to the correct value with the help of the magnification ratio and also corrected for the true breadth of component a_1 by the formula deduced by Brill.[8]

The hardness of the deposit was estimated as in our experiment with silver and our thanks are due to the authorities of the Bihar Engineering College for the use of their apparatus. Comparative values with respect to the hardness of the specimen obtained with the lowest current density, 60 in this case, are given in column 4 of table II.

There was some difficulty in making reliable measurements of the absolute hardness as boundaries of indentations were not always clearly marked and therefore relative values are given.

As the line in this particular case, has been attributed to diffracting particles of a cubic structure, the average size of crystalline particles has been calculated with the help of Scherrer's formula[9] as was done in the case of silver.

The breadth of the line for different specimens is given in table II along with relative values of hardness and average value of the size of the grain

TABLE II.

Current density in m.A. per square cm.	Indices of the line measured.	Breadth of the line.	Degree of hardness.	Average size of the grain.	Intensity of the line.	Relative. brightness.
100	110	0·28 m.m.	168	$1·72 \times 10^{-6}$cm.	100	140·30
120	,,	0·40 m.m.	183	$1·18 \times 10^{-6}$cm.	207	142·50
130	,,	0·60 m.m.	208	$0·80 \times 10^{-6}$cm	1??	122·00

7. DISCUSSION.

According to accepted view, chromium consists of body centred cubic crystals and the diffraction spectra should indicate the existence of at least 110 line which is fairly strong. We could prove that the only line obtained by us with chromium is due to the plane of indices 110.

Polanyi [10] has shown that in case of selective orientation of crystallites, there will no more be a uniform intensity distribution in the reflection cone with the incident beam as axis, as will be the case when there is random distribution of crystallites and in consequence there must ensue strong deviation of intensity according to selectivity of orientation. F. Kirchner, [11] in support of the above fact, records the deviation of intensity of 111 and 200 lines of aluminium, which is caused by different orientation of crystallites. He also records the suppression of 220 line when the Al foil is so orientated that the direction of rolling is normal to the axis of the cylindrical camera.

On examining the intensity of 110 line for different current densities, it will be observed that the intensity of the line for current density 100 m.A. is very weak compared with the intensity of the same line with current densities, 120 and 130. Also, as has been stated earlier, no visible indication of the line could be obtained with specimens of current densities 80 and 60 although the time of exposure was pushed to 20 hours. In the process of electrodeposition, there is then selective orientation of crystallites, quite in agreement with our observation with silver and the observation of Wood. [12]

We should confess that our choice of copper target was not a happy one as there is a likelihood of a little blackening of the film to be caused by the characteristic radiation which will be excited in chromium by the intense

Kα radiation of copper. However an inspection of the general blackening in figure 2 shows that the effect, if any, was certainly not sufficient to obscure other lines. Suppression of lines may also be due to the presence of various impurities in measurable proportion, in the specimen but chemical tests made, have shown that there is hardly any impurity present in specimens used by us.

In 1926, Bradley and Ollard [5] reported that in electrodeposited chromium there was presence of allotropy. They stated that atoms formed a structure, which was almost hexagonal and they gave inter-planer spacings for various lines, of which the diffraction line (1011 as recorded by them) had been found to be very strong. In 1927, Sillers, Jr.[13] analysed, by the powder method, the electrodeposited chromium in both the bright and burnt or grey condition and showed that no indications were obtained of an allotropic form of chromium. In our photograms, too, we could not trace an indication of any line due to hexagonal lattice in spite of there being a very strong line.

8. A NEW APPEARANCE.

Before concluding our discussion with electrodeposited chromium it is important to draw attention to an interesting peculiarity, which is noticed in all photograms obtained by us with chromium. It will be found on an inspection of figure 2, plate VIII that white lines appear at angles less than that for 110 line.

The curvatures of these lines are in the same direction as those for the black diffraction lines and the effect is maximum with the specimen of current density of 130 m.A in which also the selective orientation is considerable. Suspecting that the effect might have been due to some defect in the camera, the casette in which the film was taken, as also the paper covering of the camera, were changed. This made no difference and the effect persisted. Hence it is supposed that this peculiar effect must be associated with the specimen. As far as authors are aware, there is no previous record of this kind on any X-ray diffraction photogram. The persistence of the appearance with curvatures in the same direction as with those for dark lines leads us to suppose that these cannot be spurious.

Diffracting angles for two white lines in one photogram (130 m.A.) were found to be near about 10·3 and 16·5 degrees. Chromium was deposited on a wire of copper and both these materials possess cubic structure. Let us suppose that these white lines are due to a substance of cubic structure. The formula for diffraction states that

$$n\lambda = 2d_{hkl} \sin \cdot \qquad \qquad \dots \quad (1)$$

and d_{hkl} may be expressed as $d_{hkl} = \dfrac{\quad}{\sqrt{h^2 + k^2 + l^2}}$
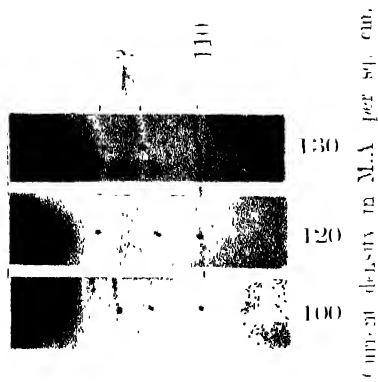
Chromium

Figure   2
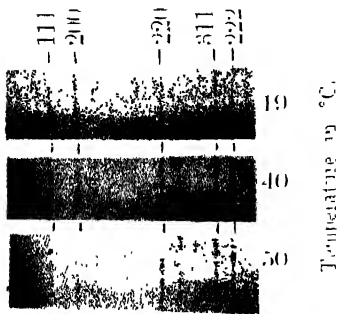
Gold

Figure   3
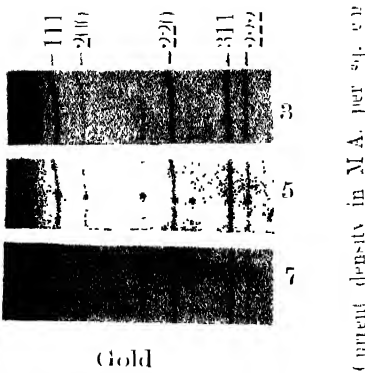
Gold

Figure   1

where a = length of cube edge

$h\ k\ l$ = Miller indices of a crystal face.

Therefore $n\lambda = 2d_{h\,k\,l} \sin\theta_n = \dfrac{2\sin\theta_n a}{\sqrt{h^2 + k^2 + l^2}}$ ... (2)

whence $\lambda^2 = \dfrac{4\sin^2\theta_n a^2}{(h^2 + k^2 + l^2)n^2} = \dfrac{4\sin^2\theta_n a^2}{h_1^2 + h_2^2 + h_3^2}$ ... (3)

where $h_1^2 = h^2 n^2, h_2^2 = k^2 n^2$ and $h_3^2 = l^2 n^2$

Equation (3) may be written in the form $\dfrac{4a^2 \sin^2\theta_n}{\lambda^2} = h_1^2 + h_2^2 + h_3^2$.

The right hand side of this equation is always integral and all but $\sin^2\theta_n$ on the left are constant for this photograph, assuming that both lines are due to a structure having the same value of a. Hence the ratio of $\sin^2\theta_n$ for any two reflections will be equal to the ratio of two integers which, at least for the most prominent lines, will be small numbers

In our case $\dfrac{\sin^2\theta_1}{\sin^2\theta_2} = 2\cdot52$ which nearly equals the ratio $\dfrac{8}{3} = 2\cdot66$. Now (h_1, h_2, h_3) values of two strong lines of a face centred cube are (111) and (220) whose $h_1^2 + h_2^2 + h_3^2$ values are 3 and 8 respectively. The value of a, when calculated on the basis of the above assumption comes out to be $7\cdot6$ Å.U. With the data available from the present experiments, it is difficult to identify this value with the structure of either of the two metals, in their usual form of crystallisation. We intend to examine this point later in details. Whatever might turn out to be the structure that gives rise to these lines, we are inclined to ascribe their appearance as absorption instead of emission lines to the process of photographic reversal.

9. GOLD

Electrodeposition of gold has been studied by the powder method by varying not only current density but also the temperature.

10. SPECIMENS.

Specimens were obtained by depositing gold on copper wires. Copper wires were put to the same preliminary treatment and cleaning as in the case of

chromium with the exception that the protecting varnish consisted of celluloid dissolved in a mixture of amylacetate and acetone. The electroplating bath was solution of the following constituents :—

Gold chloride crystals	4 grms.
Potassium cyanide	15 gms.
Distilled water ...	.500 c. c.

The anode was of extra pure gold supplied by Messrs. Leybold of Germany. No satisfactory deposit could be obtained with a current density below 3 m. A. Conditions of deposit on different specimens were identical in all respects except for variation of current densities and temperature.

While depositing at high temperatures, the concentration of the bath was maintained constant by adding distilled water from time to time so as to keep the level of the solution in the bath to the same height. Temperature was sought to be kept constant by a thermostat arrangement, but as the time of deposit of a layer of o'1 m. m. thickness was rather long, there had been slight fluctuation of temperature. Particulars of deposition are given in table III.

TABLE III.

Current density varying.   Temp. constant = 19°C.

Specimen.	Diameter of copper wire. before deposit	Current density in m A. per sq cm.	Diameter of specimen after deposit.	Time of deposit	Relative brightness.
1	o'9 mm	3	1 mm	12 hrs.	100
2	,,	5	,,	7 hrs	150
3	,,	7	,,	5 hrs.	160

Temperature varying.   Current density = 7 m. A.

Specimen.	Diameter of copper wire before deposit.	Temp. of bath.	Diameter of the specimen after deposit	Relative brightness.
1	o'9 mm	19°C	1 mm	100
2	,,	40°C	,,	128
3	,,	50°C	,,	102

Estimation of surface lustre has been made by photograghic method as in the case of chromium. In all cases, values are computed, taking the lustre of No. 1 specimen as 100. It is to be noticed that the surface brightness as measured from the density of blackening in figure 1 does not vary regularly with rise of temperature and the brightness of the specimen with current density 3 m. A. is markedly low. This is due to the fact that with such a low current density, the deposit tends to be reddish.

It has been shown by X-ray diffraction that gold consists of face centred cubic crystals and Davey[14] has shown that lines diffracted from planes of indices 111 and 311 are stronger than others. In our experiment we have examined the intensity of lines diffracted from planes 111, 220, 311, and 222 of different deposits of gold. Temperature is expected to affect the rate of deposition and different rates of deposition will grow grains of different sizes. Also it is quite possible that there would be better orientation of crystal grains with slow rate of deposition, causing variation in the intensity of resulting lines of diffraction.

II. EXPERIMENTAL.

The procedure adopted either in obtaining photograms or in measuring intensity of different diffracted lines, half-breadth, hardness and size of grains, was exactly the same as was followed in the case of silver in an earlier paper. With gold good diffraction lines were obtained with an exposure of only 10 hours.

Mean maximum values of intensity for various lines are given in table IV. The various calculated intensities were reduced in terms of the intensity of 111 lines of the first specimen of the table.

TABLE IV.

Current Density Varying. Temp Const. = 19°C.

Current density.	Plane 111.	Plane 200.	Plane 220	Plane 311.	Plane 222.	Relative brightness.
3	100·0	47·1	86·4	85·0	57·1	100
5	77·8	63·5	80·0	82·1	35·9	150
7	41·4	24·8	70·7	74·3	22·1	160

Temperature Varying.   Current Density Const. = 7 m.A.

Temperatore.	Plane 111.	Plane 200.	Plane 220.	Plane 311.	Plane 222	Relatve Brightness.
19°C	100	60·1	171·0	180·0	88·1	100
40°C	114	76·0	243·5	231·0	108·7	128
50°C	53·5	34·5	251·0	91·5	74·4	102

It is found that in cases of lines from specimens obtained with different current densities, there is diminution of intensity with increasing current density and figure 4, plate VIII shows visually also that the intensity diminishes as current density increases.

But this diminution of intensity does not follow the same course as the lustre of coatings as we have noticed with silver and chromium. It is to be remembered that silver and chromium give a white surface whereas with gold the surface is yellowish in colour which becomes brownish as the current density deminishes. Hence the photographic method and the microphotometric measurment in the usual way are not expected to yield a correct estimate of the intensity of brightness.

On comparing intensities of different diffraction lines obtained with specimens at different temperatures from figure 3 and table IV, it is noticed that the intensity variation is not regular with the change of temperature as it changes. Intensity of lines for the specimen at 40°C, surface lustre of which is maximum is the strongest whereas intensity of lines at 50°C is the weakest and lines from 111 and 200 are tending to become suppressed. In case of gold, also, it is then confirmed that there is marked variation of orientation of crystallites whenever there is variation in the rate of deposition. Again the greater intensity of lines from planes 220 and 311 as compared with that from 111 shows that so far as the degree of orientation of crystallites is concerned, certain planes are more favoured than others and in our case this favoured orientation persists even at higher temperatures, an observation recorded earlier by Kirchner [11] and Friauf [15] with metals raised to high temperature.

Diffraction picture of figure 3 has been obtained with specimens electrodeposited in baths of different temperature and it is observed that lines at higher temperatures are interspersed with spots, proving that crystallites have grown in size with rise of temperature of the bath. This observation is also similar to that of Kirchner and Friauf, who experimented with Al and molybdenum at higher temperatures and it supports also the axiom of Bancroft that lowering the temperature decreases the size of crystals.

In the following table is given the breadths of different lines, corrected by Brill's formula, along with comparative values of hardness and average value of

the size of the grain. Hardness is given in terms of the hardness of the specimen of current density 5 m.A as 100.

TABLE V.

Current density	Plane III.	Plane 200.	Plane 220.	Plane 311.	Plane 222.	Degree of hardness.	Average size of the grain.
5	0·34 mm.	0·24 mm.	0·34 mm.	0·40 mm	0·36 mm.	100	1·6 × 10⁻⁶ cm.
3	0·36 mm	0·32 mm.	0·38 mm	0·50 mm.	0·40 mm.	104	1·35 × 10⁻⁶ cm.
7	0·48 mm,	0·38 mm.	0·42 mm.	0·56 mm.	0·44 mm.	112	1·2 × 10⁻⁶ cm.

From a study of table V it is noticed that here also no regular relation has been established between the degree of orientation and hardness but the breadth of lines increases as the hardness increases. Thus our observation in case of silver, gold and chromium confirms an association between the broadening of the spectral lines and the hardness of a metal.

An increase in the value of half breadths is expected as the angle of diffraction increases but an irregularity is noticed in our measurement and this persists in all specimens. This leads us to think that particles of a particular size are orientated more favourably to give rise to one particular crystal face than another. Similar variation was also noticed by us with silver.

In conclusion, we beg to offer our heartfelt thanks to Prof. K. Prosad, B.A. (Cantab), I.E.S., for his helpful discussion and encouragement during the progress of the work. He has also been kind to go through the manuscript. We also thank our colleague, Mr. B. N. Ghosh, who has taken microphotograms for us.

Note added in proof :—W. A. Wood, in his paper on the Lattice dimensions of Electroplated and Normal Chromium (Phil. Mag., May,, 1937) has referred to the extremely diffuse nature of diffraction lines from bright electroplated chromium ; it may be that the absence of many lines on our plate is due to this reason.

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FREE ROTATION IN THE OXALATE GROUP AND THE RESONANCE BOND OF CARBOXYL.

By JAGANNATH GUPTA.

Plate IX.

ABSTRACT. The existence of axial rotation of the oxalate group about the $C-C$ axis, postulated from an analysis of the modes of vibration of the group by the author in a previous paper, is confirmed by showing that the sharp Raman line at 1300 wavenumbers observed in the spectra of the oxalates in solution, which is "forbidden" in Raman effect if the ion remains rigidly planar, is totally absent in the spectra of the solids where the ion is known to remain planar in several oxalates from results of X-ray analysis. The hypothesis of free rotation is preferred to a limited axial oscillation about the V_k configuration. The band at 1620 wavenumbers is identified with the anti-symmetric vibration ω_1 of the ionised carboxyl group $\left(-C\begin{smallmatrix}O\\\\O\end{smallmatrix}\right)^-$, and connecting this with the crystal structure data for the $O-C-O$ angle, the value of the resonance bond $(C-O)$ is calculated. The value is intermediate between single and double bond values, but approaches more towards the single bond.

The classical method of structural formulation of organic compounds does not specify any particular configuration in cases where axial rotation of groups is apparently possible about a single bond, e.g., in molecules like H_3C-CH_3, $Cl_2HC-CHCl_2$, HO_2C-CO_2H, $Cl_3Si-SiCl_3$, etc, but presupposes completely free rotation about these axes. Such a presupposition is, however, true only in a very limited number of cases ; for, in most of these molecules, the free rotation is hindered by the mutual interaction of the groups.[1] The potential energy values at different positions which such a molecule may assume during the axial rotation can be calculated by the quantum mechanical method developed by Slater,[2] and the maximum difference between the two extreme values is often found to exceed kT at room temperatures (ca. 600 calories per mole) which indicates considerable restriction of rotation. Even in a molecule like ethane, where free rotation about the $C-C$ axis was accepted definitely,[3] the experimental determination of entropies from calorimetric measurements[4] and its comparison with the values obtained from statistical mechanical[5] and perturbation[6] calculations indicate the existence of a potential barrier of well over 2000 calories per mole, thus restricting to a high degree any internal rotation of the methyl groups.

It is thus apparent that such an axial rotation of groups about a single bond is more often restricted than allowed. When, therefore, in attempting to analyse the modes of vibrations of the oxalate group from the observed Raman frequencies, it was pointed out[7] that in the aqueous solutions, the oxalate ion $\left(\begin{array}{c}O\\O\end{array}\!\!\!>\!\!C\!-\!C\!<\!\!\!\begin{array}{c}O\\O\end{array}\right)^{=}$ does not always maintain the V_h symmetry observed in the crystals of several oxalates,[8] the suggestion was unusual and waited confirmation. The reason for this extraordinary statement was that the sharp and intense line 1304 observed in the spectra of the oxalate solutions, and whose origin could be ascribed to no other mode of vibration of the oxalate group than the symmetrical one (fig. 1), is, from polarisability considerations, a forbidden line in Raman effect,
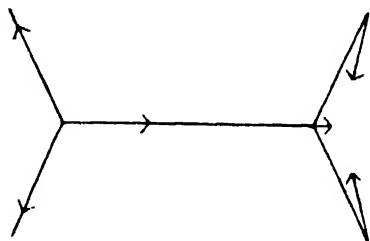
FIGURE 1.

if the ion is assumed to maintain the symmetry V_h. In order to explain the observed high intensity of the line, the hypothesis was advanced that in solution the V_h symmetry is non-existent, owing to axial rotation of the .(COO) groups about the axis $C-C$, with the result that the nett change of polarisability is considerable.

This hypothesis of free rotation, it was argued, could be tested by examining the Raman spectra of oxalates under conditions where such a rotation is impossible, *viz.*, in the crystalline state at room temperature which is far below the melting point, and comparing the intensities of the Raman lines recorded in the two different states,—the line 1304 in particular, whose very origin in Raman effect is associated[7] with free rotation of the COO groups.

In the present investigation, therefore, the spectra of two typical oxalates, potassium and ammonium, have been examined both in the solid state and in solution. The configurations of the oxalate group are known in these two cases from results of X-ray analysis, being planar in one,[8] and the (COO) planes being inclined to each other at $28°$ in the other.[13] The alkali oxalate solution is examined at two different temperatures to observe any effect due to rise of temperature on the scattered spectrum.

A second point of interest that has been raised and discussed in the present paper is the nature of the binding forces between the carbon and oxygen atoms in the ionised carboxyl group $(-COO)^{-}$. It is well-known that the salts of carboxy-

lic acids completely fail to exhibit the normal characteristics of the carbonyl group, assumed to be present in the molecule from classical concepts of valency, viz., $\left(-C\begin{subarray}{c}\diagup O\\ \diagdown O\end{subarray}\right)^-$, both from the standpoints of reactivity and unsaturation. Examinations of their Raman spectra have revealed the remarkable fact that the line 1720 wavenumbers, which is normally strong, and is attributed to the inner vibration of the C = O group, is *totally* absent, although present with its usual intensity in the esters. Results of X-ray analysis have often indicated equivalence of both the oxygen atoms with respect to carbon [8],[22] while differences in the distances recorded in some cases[13] are only slight, and apparently within the limits of experimental error. The group therefore appears to exhibit a true resonance between (C−O) and (C=O) groups, In the present paper, an attempt has been made to identify some of the observed Raman lines of the salts with the modes of vibration of the $\left(-C\begin{subarray}{c}\diagup O\\ \diagdown O\end{subarray}\right)^-$ group, where the thick line represents the resonance bond in place of either the single or the double bond, and hence a value of the force of resonance, assuming equivalence of the two bonds, has been calculated with the help of the valence force system.

EXPERIMENTAL.

Recrystallised lumps of transparent polycrystals of potassium and ammonium oxalates were obtained by sieving and hand-picking from large amounts of recrystallised samples. The spectrograms were recorded by the method of complementary filters. [9]

The aqueous solutions (nearly saturated) were prepared with usual precautions from the purest samples, freshly recrystallised. The spectrogram of the solution of potassium oxalate was recorded at two different temperatures: one at room temperature ($31°C$) and the other at $96°C$ with the help of a cylindrical electric heater which surrounds the Wood's tube on all sides but one to receive incident radiation from a quartz mercury arc. The relative intensities of the lines in the two spectrograms were compared and found to remain unchanged.
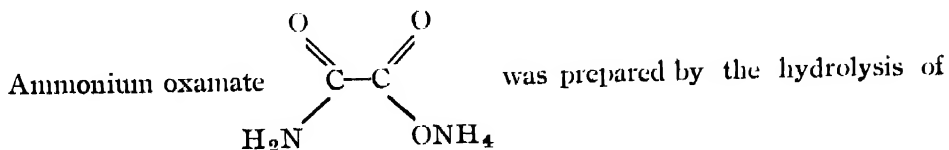
Ammonium oxamate $\begin{array}{c} O \quad\quad O \\ \diagdown\quad\diagup \\ C-C \\ \diagup\quad\diagdown \\ H_2N\quad\quad ONH_4 \end{array}$ was prepared by the hydrolysis of oxamethane [10] with strong ammonia. The free acid was precipitated by acidification with hydrochloric acid, and its purity confirmed by the melting point ($210°C$, with decomposition). The free acid was suspended in pure redistilled

water and ammonia gas was bubbled through the suspension, when the acid dissolved with the formation of the ammonium salt. The solution was filtered and filled into the Wood's tube with usual precautions.

The results are tabulated below, and some of the spectrograms are reproduced in Plate IX.

Raman Lines in wavenumbers per cm. Figures in parantheses indicate relative intensities of lines (visual).

Potassium oxalate.		Ammonium oxalate.		Ammon oxamate. Solution.
Crystals †	Solution.	Crystals.†	Solution.‡	
	295(1)			
	452(2)			133(1)
885(1)	808(2)			815(1)
			1300(1)	1085(1b)
	1305(3)			1305(4)
1442(1)	1460*(4)	1451*(3)	1465*(2)	1415*(4)
				1620(2b)
		2885(3b)		1690(2)
		2000(3b)		
			3175	3175
			3395	3395

DISCUSSION OF RESULTS.

(A) *Free Rotation.*

It can be seen from the preceding table, as well as from the spectrograms reproduced in Plate IX, that the line 1304 of the oxalate ion, which is extremely sharp and intense in the spectrum of the solution, is totally absent in that of the solid state. This cannot be due to an insufficiency of exposure in the case of the solid because, in the case of the solutions where the line 1304 is visible, the 1460 doublet is recorded with less intensity than in the solid: nor due to any fall of

* Close doublets.
† (500-1500) and (1800-4000) wavenumbers.
‡ For a more complete data (lines in other regions), see Gupta, *Ind. J. Phys.*, **10**, 199 (1936).
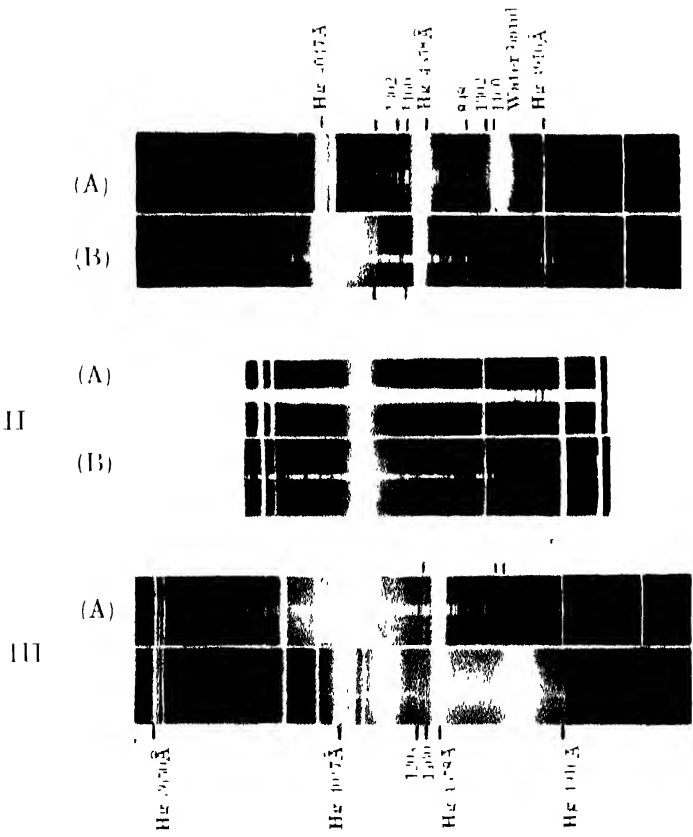
Raman Spectra.

I   (A) Potassi   Oxalate solution in water
     (B)   '   ''   crystals.

II   (A)   solution at room temperature (31 C)
                                 solution at an elevated temperature
                                                              (96 C)

III (A) Ammonium Oxalate crystals.
     (B)   ''   ''   solution in water.

sensitivity of the plate used for photographing the spectrum of the solid, in the region of $\Delta\nu1300$ cm^{-1} (exciting radiation Hg 4047Å), because the same variety of plates (Ilford's Special Rapid, H and D 270) was used for recording the spectrograms of both solids and their solutions. This fact therefore clearly confirms the view [7] regarding the existence of axial rotation of the (COO) groups in the oxalate ion in solution.

Similar conclusions were arrived at by Martin and Partington [11] from measurements of the dipole moment of oxalyl chloride. From a comparison of the experimentally determined value with theoretically deducible values by Zahn's method, [12] they postulate the existence of free rotation or axial oscillation of the COCl groups about some stable form. In the present case of the oxalate ion in solution, the hypothesis of free rotation is preferred to that of a limited axial oscillation about the V_h configuration, for the following reasons :—

(1) In the spectrogram of crystalline oxalate, where the planes of the molecule are known [13] to be inclined to each other by 28°, the line 1304 is not recorded with any appreciable intensity, showing that a slight departure of the oxalate ion from the V_h configuration is not sufficient to explain the intensity of the said Raman line.

(2) The relative intensities of the Raman lines of the spectrum of potassium oxalate solution remain unchanged at two different temperatures. If axial rotation of the (COO) groups were restricted to any extent at room temperature, an elevation of temperature would have augmented this rotation, resulting in an increase in the intensity of the line 1304 as compared to other Raman lines of the spectrum.

The substitution of one of the carboxyl group by $-C{\displaystyle {\diagup O \atop \diagdown NH_2}}$ interferes greatly with the intra-molecular rotation as may be seen from the vanishing intensity of the 1304 line in the spectrum of the oxamate. The restriction of intramolecular rotation due to the presence of the amino group is noteworthy, and have been observed by Choudhuri [14] also.

(B) *The force of Resonance* $\left(-C{\displaystyle {\diagup O \atop \diagdown O}}\right)$
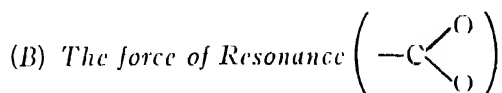
It can be observed, on comparing the spectrograms of potassium and ammonium oxalates in the solid state and in solution, that, apart from the variation of intensity of the line 1304 in the two states, other lines attributed to vibrations of the C_2O_4 group, *e.g.*, 898 and 1460, do not undergo any considerable change of position, so that the structure of the group may be assumed to be essentially the same in both the states. The X-ray data for ammonium oxalate crystals [13] and the spectral data for its solution can therefore be correlated.

The method of calculation here adopted, *viz.*, the acceptance of certain frequencies as inner frequencies of a portion of a molecule, is quite in accord with empirical observations, and is not in conflict with some of the methods recently developed.[15] A simple calculation is here made on this basis for determining the magnitude of the resonance force of the ionised carboxyl, from the value of α known accurately from X-ray analysis,[13] and the result may not be expected to be greatly in error.[16]

The anti-symmetric vibration ω_1 of the $\left(-C\diagdown_O^O\right)^-$ group is identified with the Raman line $\triangle \nu$ 1620, for the following reasons—

(1) The line remains in the same region in all the three ions $\left[\substack{O \\ O} \diagdown C - C \diagdown_O^O\right]^=$, $\left[\substack{O \\ H_2N} \diagdown C - C \diagdown_O^O\right]^-$ and $\left[Cl_3C - C \diagdown_O^O\right]^-$, the ions of oxalic, oxamic and trichloracetic [17] acids respectively, with the same character (very broad) and relative intensity (weak).

(2) The line is observed to be totally depolarised, and is therefore not of the same origin as the 1720 line of the ketones and other carboxyl compounds. This latter frequency, which is attributed to the inner oscillation of the $(C=O)$ group, gives rise to a Raman line usually polarised to a considerable extent.[18] The polarisation character of the line 1620 therefore indicates an anti-symmetric nature of the vibration in which it has its origin.

(3) The 1620 line of the oxalates is identified with ω_1 for a single ionised carboxyl group because, in the mode of vibration representing the origin of this line (fig. 2),

FIGURE 2.

$(\omega \text{ IV})^7$

it may be observed that the vibration of each of the (COO) groups is not greatly affected by the mass of the other, the resultant motion of the carbon atoms being perpendicular to the C—C axis of the molecule. Each half of the

molecule is executing an antisymmetric vibration, without any apparent mutual interference.

The antisymmetric vibration frequency, ω_1, of the ionised carboxyl group $\left(-C\begin{subarray}{l}\diagup O\\\diagdown O\end{subarray}\right)$ is deduced to be 1620 on the preceding arguments. The angle $O-C-O=129°$, from Hendricks and Jefferson's measurements.[13] The determinantal equation (valence force system) for linear, symmetric, triatomic oscillators correlating the above constants is[19]

$$n_1{}^2 = \frac{f}{m} \left\{ \frac{m}{M} \, (1+\cos a)+1\right\}$$

where $n_1{}^2 = \frac{4\pi^2 c^2}{L} \, \omega_1{}^2$, c being the velocity of light and L the Loschmidt number

$$= 5\cdot863 \times 10^{-2} \, \omega_1{}^2,$$

f = elastic force between carbon and oxygen atoms,

m, M = atomic weights of oxygen and carbon respectively,

a = supplement of the angle $O-C-O$

$$= 51°,$$

which gives the value of

$$f = 7\cdot7 \times 10^5 \text{ dynes per cm.}$$

The force constant for the single bond $(C-O)$ is 5×10^5, and for the double bond $(C=O)$ $10\cdot9 \times 10^5$ dynes per cm., accepting Kohlrausch's values.[20] The force of linkage is thus undoubtedly a resonance force, resonating between $(C-O)$ and $(C=O)$ values, but approaches the character of a single bond, as was suggested by Peychès[21] on empirical evidences. The very broad nature of the 1620 band (nearly 50 wavenumbers) indicates that the force has not a very sharp value, but is varying within narrow limits $(7\cdot4—8\cdot0)$, as may be the case during resonance.

The Badger relation [3] connecting the value of the force constant with interatomic distance, *viz.*,

$$r_e = (C_{ij}/k_e)^{\frac{1}{3}} + d_{ij},$$

where r_e = the equilibrium internuclear distance,

k_e = the bond force constant,

and C_{ij} and d_{ij} are constants, the values of which depend upon the positions of the constituent atoms in the periodic table, gives

$$r_e = \frac{\cdot571}{(\cdot77)^{1/3}} + \cdot68 = \cdot62 + \cdot68 = 1\cdot30\text{Å}$$

for the distance C—O. Pauling's value[22] from X-ray analysis of basic beryllium acetate is 1.29 Å, and is therefore in agreement with the value calculated from the spectral data.

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DERIVATION OF THE LATENT HEAT EQUATION FROM THE PRINCIPLES OF DILUTE SOLUTION.

BY B. N. BISWAS.

In the present paper, an attempt has been made to deduce the latent heat equation $\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}$ where L is the latent heat absorbed by unit mass of a substance in passing from the solid to the liquid state or from the liquid state to the state of vapour without any change of temperature, v_2 and v_1 are the specific volumes in the final and initial states. I do not claim here to derive the formula in a simpler way than that given in ordinary text books but have tried to deduce the same from another view point. Every liquid is supposed to be a solvent which can hold a non-volatile solute in solution. This solute in the dissolved state exerts a pressure called osmotic pressure like gases and obeys the gas laws, its volume being equal to the volume of the solvent, its temperature to the temperature of the same solvent. We shall further suppose that the solution is so dilute that further addition of the solvent does not produce any heat effect. Work done due to osmotic pressure owing to the addition of a small quantity of the solvent isothermally and reversibly has been calculated from two considerations and the two expressions thus obtained are finally equated which gives the above equation.

First consideration.

A small quantity of the solvent is allowed to pass from the condition of solution to the condition of saturated vapour, from the condition of vapour to the condition of pure solvent and from the condition of pure solvent to the condition of solution, isothermally and reversibly.

According to the second law of thermodynamics, total work done must be equal to zero which will contain an expression giving the work done due to osmotic pressure due to the addition of small quantity of solvent.

Second consideration.

A small quantity of the solvent is allowed to undergo a reversible cycle which consists of two isothermal processes corresponding to two infinitely close

temperatures connected by two short lines along which the same has been heated under constant pressure.

Total work done during the cycle,

$$= \text{heat absorbed at the higher temperature} \times \frac{d\mathrm{T}}{\mathrm{T} + d\mathrm{T}}$$

$d\mathrm{T}$ denotes the difference in temperatures of the two isothermal processes. The equation will contain a term giving the work done due to osmotic pressure.

Work term in the former case is equated to the work term in the latter case.

Before going directly into the problem, it is essential to prove that the latent heat absorbed by a substance in passing from the liquid state to the other is equal to that absorbed by the same substance at the same temperature in going from the state of solution to the vapour state, the pressure of the vapour being equal to the equilibrium pressure over solution which is less than the equilibrium pressure over pure solvent.

Vessel I   Vessel II
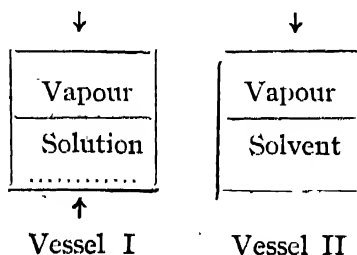
Let us consider two vessels, at the same temperature, one containing the solution in which the vapour pressure is p, the other, pure solvent, in which the vapour pressure is p_0, $p_0 > p$, p_0 being the saturation pressure corresponding to the temperature.

If we start from pure solvent in vessel II and come to the condition of saturated vapour in vessel II, through vessel I, heat absorbed and external work done during the process must be equal to the heat absorbed if we pass from pure solvent in vessel II to the condition of saturated vapour in the same vessel direct.

This is proved in the following way :

Let us start from pure solvent contained in another vessel III at temperature $\mathrm{T} + d\mathrm{T}$, where T is the temperature of the vessel I or II.

The following cyclic operation is performed.

(1) A quantity of dx grammes of the solvent is evaporated isothermally and reversibly from vessel III.

$L''.dx = $ Heat absorbed.

External work $= p'v'$ is done by the solvent where p' is the saturation vapour pressure temperature $\mathrm{T} + d\mathrm{T}$, $x' = $ difference between the volumes which the quantity dx grammes occupies in the condition of vapour and liquid.

(2) The same quantity of vapour is cooled from $\mathrm{T} + d\mathrm{T}$ to T and added without any kind of work to vessel II.

Heat eliminated $= \mathrm{K}.dx.dt$

which is of the second order, small work term being neglected,

(3) The quantity dx grammes in vessel II is then condensed isothermally and reversibly.

Heat eliminated $= L.dx.$

···Work is done on the system.

(4) Liquid thus formed is then heated from T to $T + dT$.

Heat absorbed $= K'.dx.dt$

which is of the second order, work term being neglected.

From the second law of thermodynamics we get,

Work done by the system,

$$= L''.dx. \frac{d'T}{T + d'T}. \qquad \text{... (1)}$$

Starting from vessel III, instead of completing the return path through vessel II, the same may be completed through vessel I.

Work done by the system

$$= L''.dx. \frac{d'T}{T + dT} \qquad \text{... (2)}$$

as the efficiency of a reversible heat engine is independent of the nature of the working substance.

From (1) and (2) it follows, that heat eliminated at temperature T if the return path be completed through vessel II

= heat eliminated if the return path be completed through vessel I

= heat absorbed in passing from the condition of pure solvent to the condition of saturated vapour at T through vessel II

= Latent heat of evaporation at that temperature $\times dx$ ... (3)

= heat absorbed in passing from the condition of pure solvent to the condition of saturated vapour at T through vessel I, ... (3a) and that external work done in the latter two processes must also be equal.

External work done in the former process

$$= (p + dp)(v_2 - v_1)dx \qquad \text{where } v_2 \text{ and } v_1 \text{ are specific volumes, where } p \text{ is}$$
the equilibrium pressure over solution at temperature T.   ... (4)

External work done in the latter process :

(*i*) A quantity of dx grammes of solvent is added reversibly and isothermally through the semipermeable membrane.

$$\text{Work done by the system} = P \times dv \qquad \qquad \dots \text{(5)}$$

where P is the osmotic pressure and dv is the volume which the quantity dx grammes occupies in the liquid state.

(*ii*) Isothermal and reversible evaporation of dx grammes of solution entails an amount of work done by the system

$$= p(v'_2 - v_1)dx$$

$$= p.v'_2.dx - p.v_1.dx$$

$$= p.\frac{p + dp}{p}.v_2 dx - p.v_1.dx$$

$$[(p + dp) v_2 = p.v'_2 \qquad \text{if the vapour obeys gaseous law}]$$

$$= (4) \text{ neglecting second order terms} \qquad \qquad \dots \text{(6)}$$

where v'_2 is the volume of unit mass of vapour under the pressure p and temperature T.

(*iii*) Work done on the system in compressing the vapour of dx grammes

$$\text{from } p \text{ to } p_0 = - dx \, RT \, \log_e \frac{p_0}{p} \qquad \qquad \dots \text{(7)}$$

where R is the constant for unit mass.

$$\left[\text{work done} = \int_p^{p_0} p.dv = - \int_p^{p_0} v.dp = - dx \, RT \, \log_e \frac{p_0}{p} \right]$$

As equation (4) and (6) are equal, we get,

$$P.dv - dx \, RT \, \log \frac{p_0}{p} = 0. \qquad \qquad \dots \text{(8)}$$

Now we shall prove L = L', where L' denotes the heat absorbed by unit mass of solution in passing from the condition of solution to the condition of vapour at temperature T in vessel I and L denotes the latent heat or heat absorbed by unit mass in passing from the condition of pure liquid to the condition of saturated vapour at temperature T in vessel II.

From (3) and (3a) we get,

L.dx = heat absorbed by dx grammes in passing from solvent to the condition of saturated vapour at T in vessel II through vessel I.

$$= P.dv + L'.dx - dx.RT \log \frac{p_0}{p}. \qquad \qquad \text{...} \quad (9)$$

From (8) and (9) we get,

$$L = L' \qquad \qquad \text{...} \quad (10)$$

where L' is the latent heat of evaporation of a solution.

L = L_e + external work done where L_e is the internal work done in evaporating unit mass of pure solvent at temperature T.

L' = L_e' + external work done, where L_e' = internal work done in evaporating unit mass from solution.

As L = L' and external work done in both the cases are equal we get,

$$L_e = L_e' \qquad \qquad \text{...} \quad (11)$$

WORK DONE DUE TO OSMOTIC PRESSURE FROM FIRST CONDIDERATION

A vessel is taken containing a dilute solution of which the solvent is the
liquid the latent heat equation of which, is to be derived.
Vapour   The vessel is maintained at a temperature T at which it
Solution   boils under pressure p, The vessel is provided with a piston
p   at the bottom furnished with a semipermeable membrane,
                   which allows the liquid to pass through but not the solute.

↑

The following isothermal cyclic and reversible process is imagined.

1. A quantity dx grammes of the solvent is vaporised at temperature T.

Quantity of heat absorbed = L.dx.

2. This mass of vapour is then separated without any kind of work from the vessel and compressed reversibly and isothermally from

$$p \text{ to } p + \frac{dp}{dT}.dT \quad \left[\left(\frac{dp}{dT}\right)_T - dT = \left(\frac{dp}{dT}\right)_T \text{ neglecting first order terms} \right]$$

where dT is the rise of boiling point.

Work done on the system

$$= - dx.\ RT \log \frac{p + \frac{dp}{dT}.dT}{p} \qquad \qquad \dots \ (12)$$

assuming that vapour obeys gaseous laws.

3. The same quantity for vapour is then condensed reversibly and isothermally to liquid.

$$L.dx = \text{heat eliminated.} \qquad \qquad \dots \ (13)$$

This amount of liquid is then reversibly and isothermally added to the vessel through the semipermeable membrane.

Work done by the system (as the piston is pulled out)

$= P.dv$ where P is the osmotic pressure and dv is the volume which the amount dx grammes of vapour occupies in the liquid state.

Net work done during the process,

$$= - dx.RT \log_e \frac{p + \frac{dp}{dT} \cdot dT}{p} + P.dv = 0$$

as the whole cyclic process is isothermal.

Hence we get,

$$dx.RT \log_e \frac{p + \frac{dp}{dT} \cdot dT}{p} = P.dv$$

or,
$$dx.RT. \frac{\frac{dp}{dT} \cdot dT}{p} = P.\ dv \qquad \qquad \dots \ (14)$$

For
$$\log \frac{p + \frac{dp}{dT} \cdot dT}{p} = \log \left(1 + \frac{p + \frac{dp}{dT} \cdot dT - p}{p} \right)$$

$$= \frac{\frac{dp}{dT} \ dT}{p} \qquad \text{neglecting terms of higher orders.}$$

RELATION BETWEEN WORK DONE DUE TO OSMOTIC PRESSURE FROM SECOND CONSIDERATION AND THE RISE OF BOILING POINT.

The relation is derived in the following way[*] :—

Two vessels I and II are taken. Vessel I contains solution at temperature T, its boiling under the pressure p and vessel II pure solvent at temperature T_0 under the same pressure p. $T > T_0$.
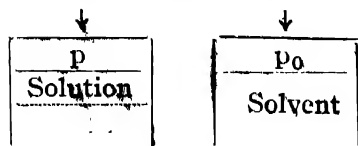
$$T - T_0 = dT.$$

Following reversible cycle is carried out :

Let   L   denote the latent heat per gramme of solvent.

       K   denote the specific heat of vapour.

       K'   denote the specific heat of solvent.

(1) A quantity dx grammes of solvent is vaporised from the solution at temperature T.

$$\text{Heat taken from the surrounding} = L.dx. \qquad \dots (15)$$

External work done by the system $= p. \, dv$; it should be noted here that L includes the heat required to do the external work.

(2) The quantity dx of vapour is now cooled to T_0.

$$\text{Heat given out} = K.dx.dT. \qquad \dots (16)$$

(3) The vapour is now condensed in vessel II reversively and isothermally.

$$\text{Heat eliminated by the mass} = -L'dx, \qquad \dots (17)$$

where $L' < L$ as L depends on temperature.

Work done on the system

$$= -p. \, dv \text{ up to first order.}$$

(4) The quantity dx now in the form of liquid is separated without work from the vessel II by sliding shutter across. The same mass dx is heated to T.

$$\text{Heat absorbed} = K'dx.dT. \qquad \dots (18)$$

[*] A System of Physical Chemistry by Lewis, p. 131, Vol. II, 4th Edition.

(5) Finally, at temperature T the mass dx (which occupies the volume dv) of the liquid solvent is added reversibly and isothermally through the semipermeable membrane.

Work done by the system $= P.dv.$ ... (19)

Heat given by (18) and (16) are neglected for though K and K' differ considerably, they are of the second order while others are of the first order.

External work done by the system $= p.dv - p.dv + P.dv$

$$= L.dx - L'.dx = P.dv. \qquad (20)$$

On applying second law, we have

$$\frac{L.dx - L'.dx}{L.dx} = \frac{dT}{T} . \qquad ... (21)$$

From (19) and (21) we get

$$P.dv = L. \; dx. \; \frac{dT}{T} . \qquad ... (22)$$

Equating (22) and (14) we get,

$$\frac{L.dx.dT}{T} = \frac{RT}{p}. \; dx \left(\frac{dp}{dT} \cdot dT \right) \; \text{or} \; \frac{L}{T} = V. \frac{dp}{dT} \qquad ... (23)$$

it being supposed that the vapour obeys gaseous laws.

V is the volume of unit mass of vapour under pressure p, the volume which unit mass of saturated vapour occupies at T is slightly smaller than V as p is slightly less than the saturation pressure corresponding to the temperature. This variation is neglected. The latent heat equation which applies to the change of state of a substance from the liquid to the vapour is,

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)},$$

where v_2 is the volume of unit mass of saturated vapour at temperature T, v_1 that of unit mass of liquid. As $v_2 >> v_1$, v_1 is neglected and the latent heat equation is put in the following form

$$\frac{L}{T.v} = \frac{dp}{dT} \quad \text{which is the same as (23).}$$

It will not be out of place to mention here that if the latent heat equation $\dfrac{L}{T.V} = \left(\dfrac{dp}{dT} \right)$ be assumed, the relation between the rise of the boiling point, osmotic pressure can be deduced in the following way :—

From (14) and (23)

$$\frac{dx.RT}{p} \cdot \frac{dp}{dT} \cdot dT = P.dv$$

$$= dx.\frac{RT}{p} \times \frac{L.dT}{T.V} = P.dv$$

If the vapour obeys gaseous laws,

$$\frac{RT}{p.v} = 1 \text{ and we have,}$$

$$\frac{L.dT}{T} = p.\frac{dv}{dx} \qquad \qquad \dots \text{ (23}a\text{)}$$

$$\frac{dv}{dx} = \frac{1}{\rho} \text{ where } \rho \text{ is the density of the solvent.} \qquad \dots \text{ (23}b\text{)}$$

From (23a) and (23b) we get,

$$\frac{L.\rho.dT}{T} = P, \qquad \qquad \dots \text{ (23}c\text{)}$$

where T is the boiling point of the solution.

DERIVATION OF THE LATENT HEAT EQUATION IN THE CASE OF CHANGE OF STATE FROM THE SOLID TO LIQUID.

The required equation is,

$$\frac{L}{T(v_2 - v_1)} = \frac{dp}{dT} . \qquad \qquad \text{(23}d\text{)}$$

Let us consider vessels I and II at temperature T, vessel I contains the solution, T being the freezing point of the solution under the pressure p and vessel II, pure solvent, the pressure in the same being $p + \dfrac{dp}{dT} . dT$ so that T is also the freezing point of pure solvent,

3

Solvent | The following isothermal and reversible cycle is
_____
Solution   imagined :—
ice   ice

Vessel I   Vessel II

Stage I. A very small quantity dx grammes of solution is frozen.

Amount of heat eliminated $= -L.dx$ where L is the latent heat per unit mass. External work done by the system $= p(v_2 - v_1).dx$ where v_2 and v_1 are specific volumes in the solid and liquid states respectively.

Stage II. The quantity dx grammes of ice is separated without any work from vessel I. The pressure to which it is subjected is increased from p to $p + \dfrac{dp}{dT} . dT$ isothermally and reversibly. Amount of work done is neglected as the change of volume of ice due to the change of pressure is very small.

Stage III. The same amount of ice is added to vessel II without any kind of work and allowed to melt isothermally and reversibly.

Amount of heat absorbed $= L'.dx$.

External work done on the system,

$$= -(p + \frac{dp}{dT} . dT) (v_2 - v_1).dx.$$

Stage IV. The same amount of solvent is then separated without any kind of work from vessel II and added reversibly and isothermally through the semi-permeable membrane.

Amount of work done by the system $= P.dv$ where P is the osmotic pressure and dv is the volume occupied by dx grammes of solvent.

As the process mentioned above is an isothermal reversible cycle, total external work done must be o.

Hence we get,

$$p.(v_2 - v_1).dx - (p + \frac{dp}{dT} .dT) (v_2 - v_1)dx \pm P.dv = o$$

or
$$P.dv = (v_2 - v_1).dx. \frac{dp}{dT} . dT. \tag{23c}$$

It should be borne in mind that the latent heat eliminated in passing from water to ice in vessel II is not equal to that eliminated in passing from the state of solution to that of ice in vessel I.

It can be proved from the second law of thermodynamics in the same way as has been adopted in the beginning of the paper that the difference between the two latent heats must be equal to $P.dv$ and the internal works done in both the vessels in changing from liquid to ice are the same.

WORK DONE DUE TO OSMOTIC PRESSURE FROM SECOND CONSIDERATION

* Relation between osmotic pressure P and the lowering of freezing point T of the solvent due to the presence of the solute.

water
Ice
T_0

Vessel I

Solution
Ice
T

Vessel II

Vessel 1 contains pure solvent, say water, in equilibrium with ice at the freezing point T_0. Vessel II contains an aqueous solution in equilibrium with ice at a temperature T lower than T_0 by the amount $d'T$, osmotic pressure in II being P.
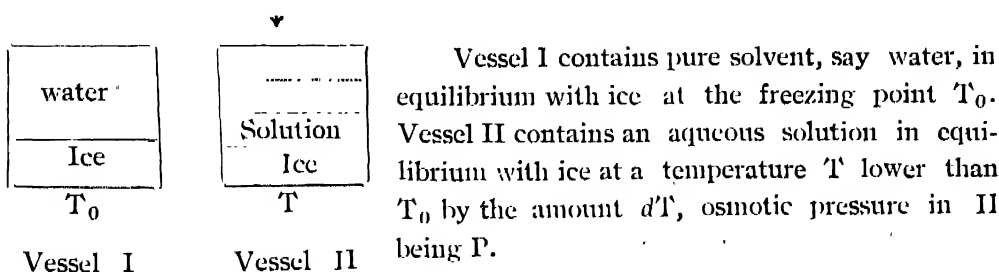
A thermodynamic cycle like the following is imagined :—

1st Stage. A small quantity dx grammes of ice is separated from vessel 1 at T_0 without any kind of work and equilibrium being established throughout. The ice is melted.

$$\text{Amount of heat absorbed} = L.dx, \qquad \qquad \dots \quad (24)$$

where L denotes heat absorbed per unit mass. In this process there is a very small amount of work done upon the system owing to the change in volume of dx.

2nd Stage. The mass dx of the water which occupies a volume dv is cooled from T_0 to T.

$$\text{Heat given out} = -K.dx\, d'T. \qquad \dots \quad (25)$$

The volume dv of water is then added reversibly and isothermally through a semipermeable membrane to the solution at the temperature T work is done by the osmotic pressure. The volume dv which the quantity dx grammes of water occupies at T_0 is nearly equal to that it occupies at T.

$$\text{External work done} = P.dv. \qquad \dots \quad (26)$$

* Lewis' Physical Chemistry, p. 133, Vol. II, 4th edition.

3rd *Stage*. A quantity dx of water is frozen out of the solution in vessel II.

$$\text{Heat given out} = -L'.dx \text{ where } L'.<L. \qquad \ldots (27)$$

In this process there is a small work term done by the system which balances the work term in the first stage.

4th *Stage*. The mass dx of the ice thus formed at T is isolated without any kind of work and raised in temperature from T to T_0 and then added without any kind of work to the vessel I.

$$\text{Heat absorbed} = K'.dx.dT. \qquad \ldots (28)$$

The algebraic sum of (25) and (28) is neglected as they are very small and of opposite sign.

The cycle is now completed.

$$\text{Nett work done by the system} = P.dv$$

$$= (L-L').dx \text{ as given by } (26). \qquad \ldots (29)$$

From the second law of thermodynamics and equation (29) we get,

$$P.dv = L.dx. \; \frac{dT}{T_0}. \qquad \ldots (30)$$

Equating (30) and (23e) we get,

$$P.dv = dx(v_2 - v_1) \frac{dp}{dT}. \; dT = \frac{L.dx}{T_0} \, dT$$

$$= \frac{L \, dx.dT}{T} \text{ as T and } T_0 \text{ are very nearly equal}$$

or $\qquad \dfrac{L}{T(v_2 - v_1)} = \dfrac{dp}{dT}$ which is the same as equation (23d).

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SPIN DOUBLING IN $^2\Sigma$ STATES OF AlO.

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Plate X.

ABSTRACT. From high dispersion spectrograms, the existence of spin doubling in both the upper and lower, $^2\Sigma$, states of the band system of AlO has been ascertained. In addition to (1, 0), (0, 0) and (0, 1) bands, which were previously analysed by Pomeroy, the structure analysis of the bands (2, 1), (1, 1) and (1, 2) has been carried out. The values of the rotational constants are in good agreement with the data of Pomeroy.

INTRODUCTION

It is very well known that the diatomic molecule, AlO, has a band system lying in the region $\lambda 4100$-$\lambda 5700$. The vibrational structure analysis of these bands was carried out by Mecke[1] in 1925 from the band head data of Möriköfer,[2] who measured them from high dispersion spectrograms. In 1927, Pomeroy[3] conducted the rotational structure analysis of three of the most intense bands, *viz.*, (1, 0), (0, 0) and (0, 1) and assigned the band system to a $^2\Sigma \longrightarrow {}^2\Sigma$ transition. In each band analysed, he observed the R and P branch lines to be double and measured each component of these doublets. He further, plotted the doublet separations as a function of the rotational quantum number, K, of the lower state and found that the doublets which are at first unresolved, increase in width almost linearly with K except towards the end where the increase is more rapid. From the equality of doublet widths in the (0, 0) and (1, 0) bands, Pomeroy concluded that the spin doubling exists mainly or entirely in the levels of the lower $^2\Sigma$ state of the band system. On the other hand one finds from the recent work of Scheib[4] and of Jenkins and Mckellar[5] on the α-system of BO and of Elliot[6] on the β-system that the spin doubling in the common lower $^2\Sigma$ level of both these systems is negligible even for high K values. In fact Elliot is definitely of opinion that the doublet separations in the β-system, which is due also to a $^2\Sigma \longrightarrow {}^2\Sigma$ transition, are chiefly due to doubling of the upper $^2\Sigma$ level. In view of this opposite behaviour of the $^2\Sigma$ states involved in the emission of the β-system of BO and of the band system of AlO under con-

sideration, one is led to infer that probably they are not the corresponding states of the two homologous molecules.

Before arriving at the above conclusion, it was thought desirable to obtain fresh data of the doublet components of the band system of AlO from high dispersion spectrograms not hitherto used with a view to study the nature of spin doubling in the $^2\Sigma$ states and to evaluate the coupling constant, which is known only in the case of a few non-hydride molecules.

In the present investigation, therefore, the structural lines of the bands (2, 1), (1, 0), (1, 1), (0, 0), (0, 1) and (1, 2) have been measured from the second order spectrograms of a 21 ft. concave grating, having a dispersion of about 0.62 A. U. per mm., which is nearly double of that used by Pomeroy.

SPIN DOUBLING IN $^2\Sigma$ STATES

In accordance with the notation used in band spectra, the designation of a molecular state depends on the value of Λ, the quantum number referring to the component of the orbital angular momentum of the electrons along the internu clear axis. Thus the molecular states are called Σ, Π, Δ, ... , for $\Lambda = 0, 1, 2...$ and are further distinguished according to the value of S, the resultant electronic spin. Hence for values of $S = 0, \frac{1}{2}, 1 ...$, a molecular state is a singlet, doublet, triplet , ... , since the multiplicity is given by $(2S+1)$. The theory underlying the behaviour of a molecular state has been much developed.

It is now well known that in a molecular state belonging to Hund's *Case-b*, the magnetic field associated with Λ is so weak that the interaction between Λ and S is small compared with the effect of the molecular rotation on the spin. Consequently S is not coupled to the internuclear axis and only Λ is quantised. The electronic orbital and the nuclear angular momenta, which are respectively parallel and perpendicular to the internuclear axis, form a resultant angular momentum, $\sqrt{K(K+1)}$, excluding the spin momentum, where K is a quantum number, whose possible values are Λ, $\Lambda + 1$, ... The nuclear angular momentum, N, due to rotation, is not a quantum number and takes the value $\sqrt{K(K+1-\Lambda^2)}$. On account of the presence of a magnetic field in the direction of K, the angular momenta $\sqrt{K(K+1)}$ and $\sqrt{S(S+1)}$ form a resultant or total angular momentum $\sqrt{J(J+1)}$ in a fixed direction, about which the coupled $K-$ and $S-$ vectors precess. Corresponding to the $(2S+1)$ different orientations of S with respect to K, the total rotational quantum number J takes $2S+1$ values. Hence for each value of K there are, in general, $2S+1$, component rotational levels differing only in J values and designated as F_1 , F_2 , F_3 , ... This type of splitting of rotational levels with a given value of K is called *Case-b spin doubling* or *trebling* according as $S = \frac{1}{2}$ or 1.

It is thus easily seen that a Σ state of any multiplicity falls into Hund's *Case-b* since it has $\Lambda = 0$. In a $^2\Sigma$ state, the resultant electronic spin corresponds to $S = \frac{1}{2}$. This interacts with the magnetic field associated with K and gives a total resultant angular momentum represented by the quantum number J, which has therefore two values, *viz.*, $J = K + \frac{1}{2}$ and $J = K - \frac{1}{2}$. If the interaction of S with K is assumed to obey the cosine law, the energy of interaction is given by

$$\tfrac{1}{2}\gamma[J(J+1) - K(K+1) - S(S+1)] \qquad \dots \quad (1)$$

where γ is the coupling constant. Each rotational level with a given value of K (except when $K = 0$) is split into two component levels designated by F_1 and F_2, where F_1 corresponds to $J = K + \frac{1}{2}$ and F_2 to $J = K - \frac{1}{2}$. From equation (1), the width of the *Case-b* spin doublet is therefore given by

$$F_1(K + \tfrac{1}{2}) - F_2(K - \tfrac{1}{2}) = \gamma(K + \tfrac{1}{2}). \qquad \dots \quad (2)$$

which shows that the component rotational levels should diverse from each other with increasing values of K, their separation increasing linearly with $(K + \frac{1}{2})$.

ROTATIONAL STRUCTURE OF $^2\Sigma \longrightarrow {}^2\Sigma$ BANDS

It has been stated in the previous section that in a $^2\Sigma$ state $(\Lambda = 0, S = \frac{1}{2})$, there is a *Case-b* spin doubling of each rotational energy level but no Λ-type doubling and that for each value of K (excepting when $K = 0$), there are two component levels, with $J = K \pm \frac{1}{2}$. For $K = 0$, there is only one level corresponding to $J = \frac{1}{2}$. Six branches are to be expected from the J, K and $+ \overleftarrow{} -$ selection rules. These are denoted as $P_1(J)$, $P_2(J)$, ${}^PQ_{12}(J)$, ${}^RQ_{21}(J)$, $R_1(J)$ and $R_2(J)$. They form two series of triple lines, one series corresponding to the P and the other to the R branch of *Case-b'*. The P series is composed of the sub-series $P_1(J)$, $P_2(J)$ and ${}^PQ_{12}(J)$, while the R series of $R_1(J)$, $R_2(J)$ and ${}^RQ_{21}(J)$. At the band origin, there is only one missing line in each of the branches $P_1(J)$ and $P_2(J)$ corresponding to $J'' = \frac{1}{2}$.

Except for the lowest values of K, the two sub-series ${}^PQ_{12}(J)$ and ${}^RQ_{21}(J)$ are of negligible intensity and very often even the first and the strongest line in each of them, *viz.*, ${}^PQ_{12}(\frac{1}{2})$ and ${}^RQ_{21}(\frac{1}{2})$ cannot be detected for lack of resolution from the much stronger lines $P_1(1\frac{1}{2})$ and $R_2(\frac{1}{2})$. Hence for all practical purposes the P and R series are composed of doublets. Except for very low values of K, the intensities of the two components in each doublet are practically equal, those of the P series being slightly higher. For low K-values, the intensities of the components of any P or R doublet are not equal, P_1 or R_1 associated with the F_1 sub-level, corresponding to $J = K + \frac{1}{2}$, being the stronger. In cases where the

doublet components are resolved for low K-values, they offer, therefore a criterion for associating them with F_1 and F_2 levels.

The wave-numbers of the lines of the six branches are given by

$$P_1 (J) = T'_1 (J-1) - T'' (J),$$

or

$$P_1 (K+\tfrac{1}{2}) = T'_1 (K-\tfrac{1}{2}) - T''_1 (K+\tfrac{1}{2});$$

$$P_2 (J) = T'_2 (J-1) - T''_2 (J),$$

or

$$P_2 (K-\tfrac{1}{2}) = T'_2 (K-\tfrac{3}{2}) - T''_2 (K-\tfrac{1}{2});$$

and

$$^PQ_{12} (J) = T'_1 (J) - T''_2 (J);$$

while

$$(3)$$

$$R_1 (J) = T'_1 (J+1) - T''_1 (J),$$

or

$$R_1 (K+\tfrac{1}{2}) = T'_1 (K+\tfrac{3}{2}) - T''_1 (K+\tfrac{1}{2});$$

$$R_2 (J) = T'_2 (J+1) - T''_2 (J),$$

or

$$R_2 (K-\tfrac{1}{2}) = T'_2 (K+\tfrac{1}{2}) - T_2'' (K-\tfrac{1}{2});$$

and

$$^RQ_{21} (J) = T'_2 (J) - T''_1 (J),$$

where, as usual, J is written for J'' and K for K''.

<div align="center">THE EVALUATION OF γ</div>

In a $^2\Sigma$ state, due to *Case-b* spin doubling of the rotational levels with a given K-value, the rotational energy terms are given approximately by

$$F(K) = B_r K(K+1) + D_r K^2(K+1)^2 + \tfrac{1}{2}\gamma [J(J+1) - K(K+1) - S(S+1)] \quad \cdots \quad (4)$$

and hence the total energy terms by

$$T(J) = T_r + G(v) + B_v K(K+1) + D_v K^2(K+1)^2 + \tfrac{1}{2}\gamma [J(J+1) - K(K+1) - S(S+1)]; \quad \cdots \quad (5)$$

so that

$$T_1(K+\tfrac{1}{2}) = T_e + G(v) + B_v K(K+1) + D_v K^2(K+1)^2 + \tfrac{1}{2}\gamma K; \quad \cdots \quad (6)$$

and

$$T_2(K-\tfrac{1}{2}) = T_e + G(v) + B_v K(K+1) + D_v K^2(K+1)^2 - \tfrac{1}{2}\gamma(K+1), \quad \cdots \quad (7)$$

giving

$$T_1(K+\tfrac{1}{2}) - T_2(K-\tfrac{1}{2}) = \gamma(K+\tfrac{1}{2}), \quad \cdots \quad (8)$$

which shows like equation (2), that the width of *Case-b* spin doublet is proportional to $(K+\tfrac{1}{2})$.

As is well known, the combination differences in the upper $^2\Sigma$ state are given by

$$\Delta_2 T'_1(J) = R_1(J) - P_1(J)$$

and

$$\Delta_2 T'_2(J) = R_2(J) - P_2(J)$$

$$\qquad \qquad \cdots \quad (9a)$$

and those in the lower $^2\Sigma$ state by

$$\Delta_2 T''_1(J) = R_1(J-1) - P_1(J+1)$$

and

$$\Delta_2 T''_2(J) = R_2(J-1) - P_2(J+1)$$

$$\qquad \qquad \cdots \quad (9b)$$

so that in any state, we have

$$\Delta_2 T_1(K+\tfrac{1}{2}) = 4B_v(K+\tfrac{1}{2}) + \gamma + 8D_v(K+\tfrac{1}{2})\ (K^2+K+1)$$

and

$$\Delta_2 T_2(K-\tfrac{1}{2}) = 4B_v(K+\tfrac{1}{2}) - \gamma + 8D_v(K+\tfrac{1}{2})\ (K^2+K+1)$$

$$\qquad \qquad \cdots \quad (10)$$

giving

$$\gamma = \tfrac{1}{2}[\Delta_2 T_1(K+\tfrac{1}{2}) - \Delta_2 T_2(K-\tfrac{1}{2})], \qquad \qquad \cdots \quad (11)$$

which offers, therefore, a method of evaluating γ in the two states involved in the transition of the band system.

In cases where it is possible to observe the first lines of the $^rQ_{12}(J)$ and $^rQ_{21}(J)$ branches, we have a second method of determining the value of γ in the two states from equations (12) given below, since

$$\gamma' = \tfrac{2}{3}[T'_1(1\tfrac{1}{2}) - T'_2(\tfrac{1}{2})] = \tfrac{2}{3}[R_1(\tfrac{1}{2}) - {}^rQ_{21}(\tfrac{1}{2})]$$

and

$$\gamma'' = \tfrac{2}{3}[T''_1(1\tfrac{1}{2}) - T''_2(\tfrac{1}{2})] = \tfrac{2}{3}[^rQ_{12}(\tfrac{1}{2}) - P_1(1\tfrac{1}{2})].$$

$$\qquad \qquad \cdots \quad (12)$$

This method, however, cannot be utilised in the present case. The first method has, therefore, been adopted and the values of $\Delta_2 T_1(K+\tfrac{1}{2})$ and $\Delta_2 T_2(K-\tfrac{1}{2})$ in the two states for different values of v are given in tables II and III.

It is further seen that the separation between the two components of P and R doublets for a given value of K is given by

$$\Delta\nu_{12}(P) = P_1(K+\tfrac{1}{2}) - P_2(K-\tfrac{1}{2})$$

$$= [T'_1(K-\tfrac{1}{2}) - T'_2(K-\tfrac{3}{2})] - [T''_1(K+\tfrac{1}{2}) - T''_2(K-\tfrac{1}{2})]$$

$$= (\gamma' - \gamma')\ K - \tfrac{1}{2}\ (\gamma' + \gamma''). \qquad \qquad \cdots \quad (13a)$$

Since $T_1(K+\tfrac{1}{2}) - T_2(K-\tfrac{1}{2}) = \gamma(K+\tfrac{1}{2})$ by equation (8).

Similarly,

$$\Delta\nu_{12}(R) = R_1(K+\tfrac{1}{2}) - R_2(K-\tfrac{1}{2})$$

$$= [T'_1(K+\tfrac{3}{2}) - T'_2(K+\tfrac{1}{2})] - [T''_1(K+\tfrac{1}{2}) - T''_2(K-\tfrac{1}{2})]$$

$$= (\gamma' - \gamma'')\ K + \tfrac{1}{2}\ (3\gamma' - \gamma''). \qquad \qquad \cdots \quad (13b)$$

4

It is evident from equations (13a) and (13b) that on plotting $\Delta\nu_{12}$ (P) or $\Delta\nu_{12}$ (R) against K, a straight line of gradient $(\gamma'-\gamma'')$ would be obtained in either case, the interval between the two curves being equal to $2\gamma'$. The value of this gradient would offer a check on the individual values of γ' evaluated by means of equation (11).

It is further seen that if the spin doubling in the upper state is zero, that is when $\gamma'=0$, the interval between the two curves vanishes. Each of the equations (13a) and (13b) is reduced to

$$\Delta\nu_{12} \text{ (P) or } \Delta\nu_{12} \text{ (R)}$$

$$= -\gamma''K - \frac{\gamma''}{2}, \qquad \ldots \text{ (14)}$$

and hence the two curves $\Delta\nu_{12}$ (P):K and $\Delta\nu_{12}$ (R):K should be coincident. On the other hand, if $\gamma''=0$, we have

$$\Delta\nu_{12} \text{ (P)} = \gamma'K - \tfrac{1}{2}\gamma' \qquad \Big\}$$

and $\qquad \Delta\nu_{12} \text{ (R)} = \gamma'K + \tfrac{3}{2}\gamma''. \qquad \Big\} \qquad \ldots \text{ (15)}$

Consequently, the two curves $\Delta\nu_{12}$ (P):K and $\Delta\nu_{12}$ (R):K would coincide only if the $\Delta\nu_{12}$ (P):K curve is shifted by two units to the right.

EXPERIMENTAL DATA

An aluminium arc similar to that described by Pomeroy has been used for photographing the bands in the first and second orders of a 21 ft. concave grating of 30,000 lines with Paschen mounting. The dispersion in the second order is about 0·62 A.U. per mm. Fine grained green-sensitive photographic plates were used in order to obtain the greatest resolution possible. In figure 1, are reproduced typical portions of the (1, 0), (0, 0) and (0, 1) bands.

The structure lines of each band were measured from both the first and second order plates with the help of a Gaertner 100 mm. comparator. Iron arc lines served as wave-lengths standards. Several sets of measurements were taken on each plate for the components of R and P doublets, where they are resolved. The mean of all such measurements was taken to calculate the wave-number value of each component. Except where there is a blending of different series of the same band or of the succeeding band, the individual measurements do not differ from one another by more than 0·02 cm.$^{-1}$ For the purpose in hand, it was not necessary to measure all the lines which can be followed in a band. In table I, are given the wave-number data of the lines measured for each band. This includes the structure lines of bands (2, 1), (1, 1) and (1, 2), in addition to those of

(1, 0), (0, 0) and (0, 1) which have been previously measured by Pomeroy from the second order plates of a 21 ft. concave grating with dispersion of about 1·33 A.U. per mm.

Table I also includes the K-value of each line and the values of combination differences calculated from the mean of the wave-numbers of the components of the R and P doublets. It may here be noted that Pomeroy has listed in his tables only the wave-number corresponding to the centre of each doublet line, although he has shown graphically elsewhere the doublet separations as a function of K. It is found that the values of these doublet centres differ from those of the present measurement by not more than 0·2 cm.$^{-1}$ in the case of (0, 0) and (1, 0) bands. For the (0, 1) band, the difference exceeds in no case by 0·08 cm.$^{-1}$ On the other hand, the values of combination differences are in good agreement with those given by Pomeroy. Consequently, the B_v- and D_v-values calculated by him remain unaltered. With the present new data of the structure lines of (2, 1), (1, 1) and (1, 2) bands, the accuracy of these values has been further confirmed. It may be further noted that adopting the present notation of K-numbering, the j-numbering of Pomeroy has been shifted by unity. The assignment of subscripts 1 and 2 to the components of R and P doublets is only provisional since no inequality in their intensity could be discerned for the K-values at which they are resolved under the present dispersion. Extrapolated values have been given for lines where there is a blending. These are marked with asterisks in Table I.

TABLE I

(1, 0) Band.

K″	R_1	R_2	P_1	P_2	$\Delta_2 T'$	$\Delta_2 T''$
17	—		21465·72		—	—
18	—		63·05		—	—
19	—		60·29		—	—
20	—		57·43		—	—
21	21505·71		54·44		51·27	—
22	05·07		51·40		53·67	57·44
23	04·33		48·27		56·06	59·07
24	03·54		21445·33	21444·87	58·44	62·45
25	02·91		42·11	41·65	60·83	64·97
26	21502·06	21501·50	38·80	38·34	63·21	67·55

TABLE I (*contd.*)

(1, 0) Band (*contd.*).

K"	R₁	R₂	P₁	P₂	Δ₂T'	Δ₂T"
27	21501·00	21500·44	21435·40	21434·93	65·56	70·09
28	499·89	499·33	31·95	31·44	67·92	72·56
29	98·73	98·18	28·41	27·91	70·29	75·08
30	97·53	96·93	24·79	24·28	72·70	77·60
31	96·19	95·59	21·11	20·60	75·04	80·16
32	94·75	94·15	17·35	16·80	77·38	82·72
33	93·18	92·58	13·45	12·90	79·71	85·27
34	91·52	90·92	09·46	08·91	82·04	87·78
35	89·81	89·16	05·38	04·83	84·38	90·29
36	88·01	87·36	01·21	00·66	86·75	92·79
37	86·12	85·47	396·99	396·40	89·10	95·29
38	84·18	83·53	92·69	92·10	91·46	97·80
39	82·15	81·50	88·29	87·70	93·83	100·34
40	80·02	79·33	83·81	83·22	96·16	102·88
41	77·81	77·11	79·24	78·64	98·52	105·39
42	75·50	74·81	74·58	73·98	100·87	107·91
43	73·10	72·41	69·87	69·23	103·20	110·40
44	70·61	69·92	65·08	64·43	105·51	112·88
45	68·07	67·34	60·19	59·55	107·83	115·37
46	65·45	64·71	55·21	54·58	110·19	117·86
47	62·73	61·99	50·16	49·52	112·52	120·40
48	59·92	59·18	45·00	44·37	114·87	122·89
49	57·02	56·28	39·81	39·13	117·18	125·37
50	54·02	53·29	34·53	— 33·84	119·47	127·84
51	50·99	50·25	29·16	28·47	121·81	130·29
52	47·86	47·07	23·70*	23·02	124·10	132·81
53	44·64	43·85	18·15*	17·47	126·43	135·29
54	41·32	40·54	12·51*	11·84	128·76	137·76

TABLE I (*contd.*)

(1, 0) Band (*contd.*).

K"	R$_1$	R$_2$	P$_1$	P$_2$	Δ_2T'	Δ_2T ''
55	21437·88	21437·09	21306·84*	21306·12	131·00	140·27
56	34·34	33·56	01·03*	00·30	133·29	142·71
57	30·75	29·97	295·13	294·41	135·59	145·17
58	27·12	26·30	89·14	88·42	137·93	147·63
59	23·40	22·58	83·12	82·35	140·26	150·10
60	19·59	18·77	77·00	76·23	142·57	152·58
61	15·69	14·82	70·80	70·03	144·84	155·06
62	11·70	10·83	64·51	63·74	147·14	157·48
63	07·62	06·75	58·18	57·37	149·41	159·91
64	03·45	02·58	51·76	50·95	151·66	162·33
65	399·19	398·32*	45·26	44·45	153·90	164·79
66	94·84	93·93	38·63	37·81	156·16	167·28
67	90·40	89·48	31·90	31·05	158·47	169·71
68	85·87	84·95	25·10	24·24	160·74	172·13
69	81·25	80·34	18·24	17·39	162·98	174·52
70	76·59	75·63	11·32	10·46	165·22	176·94
71	71·84	70·88	04·30	03·40	167·51	179·36
72	66·99	66·04	197·20	196·30	169·76	181·80
73	62·02	61·06	90·01	89·11	171·98	184·23
74	57·00	55·99	82·73	81·84	174·21	186·62
75	51·89	50·88	75·37	74·48	176·46	189·03
76	46·69	45·69	67·93	66·99	178·73	191·45
77	41·41	40·40	60·40	59·46	180·97	193·87
78	36·03	34·98	52·79	51·85	183·18	196·27
79	30·52	29·47	45·10	44·16	185·36	—
80	24·93	—	37·36	36·38	—	—
81	19·29	—	29·50	28·52	—	—
82	13·56	—	21·55	20·57	—	—

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TABLE I (*contd.*)

(1, 0) Band (*contd.*).

K″	R₁	R₂	P₁	P₂	Δ₂T′	Δ₂T″
83	21307·75	—	21113·52	21112·55	—	—
84	01·85	—	05·41	04·43	—	—
85	—	—	097·22	096·19	—	—
86	—	—	88·94	87·92	—	—
87	—	—	80·58	79·56	—	—
88	—	—	72·19	71·16	—	—
89	—	—	63·71	62·64	—	—
90	—	—	55·05	53·99	—	—
91	—	—	46·32	45·26	—	—
92	—	—	37·51	36·40	—	—
93	—	—	28·57	27·46	—	—
94	—	—	19·55	18·44	—	—

(1, 1) Band.

K″	R₁	R₂	P₁	P₂	Δ₂T′	Δ₂T″
3	—	—	20529·77*	20529·43	—	—
4	—	—	28·29*	27·95	—	—
5	—	—	26·73*	26·39	—	—
6	—	—	25·09*	24·75	—	—
7	—	—	23·36*	23·02*	—	—
8	—	—	21·59*	21·21	—	—
9	—	—	19·74	19·36*	—	—
10	—	—	17·80	17·42	—	—
11	—	—	15·82	15·44	—	—
12	—	—	13·76*	13·38	—	—

TABLE I (*contd.*)

(í, í) Band (*contd.*).

K″	R₁	R₂	P₁	P₃	Δ₂T′	Δ₂T″
13	—		20511·65	20511·28	—	—
14	—		09·51*	09·13	—	—
15	—		07·32	06·90	—	—
16	—		05·05*	04·63	—	—
17	—		02·69	02·27	—	—
18	—		00·21*	499·79	—	—
19	—		497·65	97·23	—	—
20	—		95·00*	94·58	—	—
21	—		92·31	91·85	—	—
22	—		89·54	89·08	—	—
23		20542·55	86·69*	86·23	56·09	—
24		42·00	83·75	83·29	58·48	62·01
25		41·41	80·77*	80·31	60·87	64·50
26	20540·99	20540·44*	77·75*	77·25	63·21	67·02
27	40·19	39·65*	74·65	74·14	65·53	69·50
28	39·34*	38·79	71·46*	70·96	67·85	71·98
29	38·41	37·86	68·19	67·69*	70·19	74·43
30	37·44	36·89	64·88	64·38	72·53	76·88
31	36·43*	35·88*	61·53*	60·98*	74·90	79·34
32	35·38*	34·79	58·09	57·55	77·26	81·85
33	34·24	33·65	54·58*	54·03	79·64	84·37
34	33·01	32·42*	50·98*	50·44	82·00	86·91
35	31·75*	31·16*	47·30	46·76	84·42	89·43
36	30·40	29·77*	43·58	42·99*	86·80	91·97
37	28·92	28·29*	39·77	39·19	89·12	94·44
38	27·41*	26·77*	35·93	35·35*	91·45	96·85
39	25·85	25·22*	32·05*	31·46	93·78	99·30
40	24·25	23·57*	28·08	27·50*	96·12	101·79

TABLE I (*contd.*)

(1, 1) Band (*contd.*).

K″	R₁	R₂	P₁	P₂	$\triangle_2 T'$	$\triangle_2 T''$
41	20522˙56	20521˙89*	20424˙03*	20423˙45*	98˙48	104˙32
42	20˙79	20˙12	19˙90	19˙28	100˙86	106˙85
43	18˙94*	18˙26*	15˙69*	15˙06	103˙23	109˙33
44	17˙00	16˙33	11˙44	10˙81	105˙44	111˙81
45	14˙98*	14˙31	07˙10*	06˙48	107˙86	114˙28
46	12˙92	12˙20	02˙69	02˙07*	110˙18	116˙76
47	10˙77	10˙06*	398˙19	397˙57	112˙53	119˙28
48	08˙54	07˙83	93˙62	92˙95	114˙90	121˙79
49	06˙23*	05˙51*	88˙96*	88˙29	117˙25	124˙25
50	03˙83	03˙12	84˙26	83˙60	119˙54	—

(2, 1) Band.

K″	R₁	R₂	P₁	P₂	$\triangle_2 T'$	$\triangle_2 T''$
10	—		21372˙89		—	—
11	—		70˙78*		—	—
12	—		68˙59		—	—
13	—		66˙31*		—	—
14	—		63˙98		—	—
15	—		61˙60		—	—
16	—		59˙19		—	—
17	—		56˙68		—	—
18	—		54˙08		—	—
19	—		51˙43		—	—
20	—		48˙65		—	—
21	—		45˙82*		—	—
22	—		42˙95		—	—
23	21395˙62		39˙95*		55˙67	—

TABLE I (*contd.*)

(2, 1) Band (*contd.*).

K″	R₁	R₂	P₁	P₂	$\triangle_2$T″	$\triangle_2$T″
24	21394 84*		21336 85		57·99	61·98
25	94·02*		21333·89*	21333·39	60·38	64·48
26	21393 38	21392·83*	30·61*	30·11	62·74	67·03
27	92·37*	91·82	27·25	26·74	65·10	69·52
28	91·32	90·77	23·83*	23·33	67·46	72·01
29	90·17	89·62*	20·33	19 83	69 81	74·50
30	88·94	88·34*	16·79	16·29	72·10	76·99
31	87·61*	87·01	13·15	12·65*	74·41	79·48
32	86·19	85·60	09·43	08·89	76·73	82·02
33	84·68	84·09*	05·57	05·02	79·09	84·50
34	83·13*	82·49	01·67	01.12*	81·42	86·94
35	81·48	80·84	297·72	297·17	83·72	89·41
36	79·79	79·15*	93·68	93·13	86·07	91·88
37	78·05	77·41	89·55	89·01*	88·45	94·39
38	76·22	75·58*	85·38	84·79	90·82	96·91
39	74·30*	73·62	81·12	80·53	93·14	99·42
40	72·25	71·56*	76·78*	76·19*	95·42	101·92
41	70·10*	69·41*	72·34	71·75	97·71	104·38
42	67 86	67·18*	67·81	67.23	100·00	106·83
43	65·58	64·89*	63·24	62·61	102·31	109·30
44	63·25	62·56	58·54	57·91*	104·68	111·95
45	60·88*	60·15*	53·80	53·16	107·03	114.21
46	58·37	57·63	49·01	48·38	109·31	116·74
47	55·76	55·04*	44·09	43·45	111·63	119.26

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TABLE I (*contd.*)

(2, 1) Band (*contd.*).

K″	R₁	R₂	P₁	P₂	Δ₂T′	Δ₂T″
48	21353·03	21352·30	21239·08	21238·40*	113·92	121·76
49	50·24*	49·52*	33·98	33·30	116·24	124·21
50	47·38	46·64*	28·79	28·12	118·56	126·70
51	44·46*	43·68	23·52	22·85	120·89	129·17
52	41·45*	40·67*	18·20*	17·48*	123·22	131·63
53	38·40	37·62	12·80	12·08	125·57	134·06
54	35·25*	34·48*	07·36	06·64	127·86	136·50
55	32·02	31·25	01·87	01·15	130·12	138·88
56	28·70*	27·93	196·34*	195·62	132·33	141·29
57	25·29	24·47	90·72	89·96	134·54	143·72
58	21·79	20·97	84·98	84·21	136·79	146·17
59	18·20*	17·38	79·10	78·33	139·08	148·63
60	14·51	13·70*	73·13	72·37	141·35	151·09
61	10·74	09·93	67·08*	21166·32	143·63	153·54
62	06·88*	06·07*	60·94	60·18*	145·91	156·02
63	02·98	02·12*	54·72	53·91	148·24	158·47
64	298·99	298·12	48·41	47·60	150·55	—

(0, 0) Band.

K″	R₁	R₂	P₁	P₂	Δ₂T′	Δ₂T″
2			20633·11		—	—
3			31·61		--	—
4			30·04	—	—	—
5			28·42		—	—
6			26·75		—	—
7			25·02		—	---
8			23·23		—	

TABLE I (*contd.*)

(o, o) Band *contd.*).

K″	R₁	R₂	P₁	P₂	$\triangle_2 T'$	$\triangle_2 T''$
9		—	20621·36		—	—
10		—	19·40		—	—
11		—	17·36		—	—
12		—	15·24		—	—
13		—	13·07		—	—
14		—	10·86		—	—
15		—	08·57		—	—
16		—	06·23		—	—
17		—	03·81		—	—
18		—	01·30		—	—
19		—	598·71		—	—
20		20645·04	96·04		—	—
21		44·61	20593·46	20593·16	51·73	—
22		44·10	90·66	90·32	54·12	57·44
23			87·77	87·44	56·50	59·98
24	20643·72	20643·33	84·80	84·47	58·89	62·47
25	43·07	42·65	81·80	81·46	61·23	64·99
26	42·35	41·92	78·70	78·36	63·60	67·52
27	41·58	41·12	75·53	75·15	66·01	70·05
28	40·73	40·26	72·27	71·89	68·41	72·62
29	39·79	39·32	68·92	68·54	70·82	75·16
30	38·77	38·26	65·54	65·12	73·18	77·69
31	37·66	37·15	62·07*	61·65	75·54	80·21
32	36·47	35·96	58·52*	58·09	77·91	82·71
33	35·24	34·72	54·93*	54·46	80·29	85·20
34	33·96	33·45	51·25*	50·78	82·69	87·73
35	32·60	32·04	47·49*	47·02	85·07	90·29
36	31·14	30·59	43·65*	48·18*	87·45	92·83

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TABLE I (contd.)

(o, o) Band (contd.).

K″	R₁	R₂	P₁	P₂	Δ₂T′	Δ₂T″
37	20629·61	20629·06	20539·72*	20539·26*	89·84	95·34
38	28·00	27·44	35·75	35·29*	92·20	97·86
39	26·30	25·74	31·71	31·24*	94·55	100·36
40	24·55	23·95	27·62	27·11*	96·89	102·83
41	22·72	22·13	23·45	22·94*	99·23	105·31
42	20·81	20·21	19·19*	18·69*	101·57	107·82
43	18·81	18·21	14·85*	14·35	103·91	110·35
44	16·77	16·13	10·43*	09·89	106·29	112·85
45	14·64	14·01	05·93*	05·39	108·66	115·38
46	12·43	11·79	01·35	00·80*	111·04	117·91
47	10·14	09·50	496·68	496·14*	113·41	120·41
48	07·76	07·08	91·98	91·43*	115·72	122·91
49	05·29	04·62	87·19	86·64*	118·04	125·35
50	02·79	02·11	82·36	81·78*	120·38	127·81
51	00·20	599·52	77·45	76·83	122·72	130·30
52	597·53	96·80	72·46	71·84	125·01	132·79
53	94·77	94·05	67·39	66·76	127·34	135·24
54	91·93	91·21	62·24	61·61	129·65	137·74
55	89·04	88·33	57·01	56·34	132·01	140·22
56	86·08	85·36	51·69	51·02	134·37	142·70
57	83·07	82·31	46·34	45·63	136·71	145·18
58	79·93	79·17	40·90	40·19	139·01	147·66
59	76·71	75·95	35·39	34·68	141·30	150·10
60	73·41	72·65	29·83	29·08	143·58	152·55
61	70·07	69·26	24·16	23·40	145·88	155·01
62	66·59	65·79	18·40	17·65	148·17	157·48
63	63·08	62·28*	12·56	11·81	150·50	159·90
64	59·49	58·69*	06·69	05·90	152·80	162·35

TABLE I (*contd.*)

(o, o) Band (*contd.*).

K″.	R₁	R₂	P₁	P₂	Δ₂T″	Δ₂T‴
65	20555 85	20555·01*	20400·73	20399·91	155·10	164·79
66	52·09	51·25*	394·70	93·91	157·37	167·22
67	48·25	47·40*	88·63	87 80	159·61	169·66
68	44·37	43·48*	82·43	81·60	161·91	172·08
69	40·40	39·51*	76·16	75·33	164·21	174·53
70	36·35	35·46*	69·81	68·98	166·51	176·97
71	32·21	31·33*	63 42	62·55	168·79	179·39
72	28·04	27 11*	56·95	56·08	171·06	181·81
73	23·74	22·81*	50·40	49·53	173·31	184·23
74	19·36*	18·43*	43·78	42·91	175·55	186·61
75	14·94*	13·97	37·12	36·21	177·79	189·01
76	10·39*	09·42	30·34	29·42	180·02	191·43
77	05·77*	04·80	23 47	22·57	182·26	193·82
78	01·05*	00·09	16·53	15·63	184·49	196·20
79	496·26*	495·30	09·56	08·61	186 70	198·58
80	91·43*	90·42	02 47	01·52	188·93	200·96
81	86·52*	85·51	295·29	294·35	191·19	203·35
82	81·57*	80·56	88 04	87·10	193 49	205·75
83	76·53	75·48	80·76	79·77	195·74	208·16
84	71 38	70·33	73·40	72·41	197·95	210·50
85	66·14	65·09	66·00	65·01	200·11	212·82
86	60·82	59·77	58·53	57 54	202·26	215·15
87	55·42	454·33	50·98	49·95	204·41	217·49
88	49·93	48·85	43·31	42·29	206·59	219·82
89	44·37	43·29	35·56	34·54	208·78	222·18
90	38·77	37·64	27·74	26·68	210·99	224·52
91	33·09	31·96	19·85	18·78	213·21	226·86
92	27·33	26·20	11·88	10·81	215·42	229·20

TABLE I (*contd.*)

(0, 0) Band (*contd.*).

K″	R$_1$	R$_2$	P$_1$	P$_2$	$\triangle_2$T′	$\triangle_2$T″.
93	20421·49	20420·32	20203·87	20202·77	217·58	231·56
94	15·52	14·36	195·75	194·65	219·74	233·90
95	09·48	08·31	87·55	86·45	221·89	236·25
96	03·40	02·19	79·24	78·14	224·10	238·55
97	397·19	395·99	70·89	69·79	226·25	—
98	90·91	89·71	—	—	—	
99	84·59	83·35	—	—	—	
100	78·15	76·91	—	—	—	
101	71·63	70·39	—	—	—	
102	65·08	63·79	—	—	—	
103	58·40	57·12	—	—	—	
104	51·65	50·36	—	—	—	

(0, 1) Band.

K″	R$_1$	R$_2$	P$_1$	P$_2$	$\triangle_2$T′	$\triangle_2$T″
5	—	—	—	19662·77*	—	—	—
6	—	—	—	61 22*	—	—	—
7	—	—	—	59·64*	—	—	—
8	—	—	—	57·97	—	—	—
9	—	—	—	56·24	—	—	—
10	—	—	—	54·42	—	—	—
11	—	—	—	52·53	—	—	—
12	—	—	—	50·59	—	—	—
13	—	—	—	48·59	—	—	—
14	—	—	—	46·54	—	—	—
15	—	...	—	44·42	—	—	—
16	—	...	—	42·22	—	—	—

TABLE I (contd.)

(0, 1) Band (contd.).

K″	R₁	R₂	P₁		P'₂	Δ₁T′	Δ₂T″
17	—	—	—	39·98	—	—	—
18	—	—	—	37·66	—	—	—
19	—	—	—	35·31	—	—	—
20	—	—	—	32·88	—	—	—
21	—	—	—	30·37	—	—	—
22	—	—	—	27·83	—	—	—
23	—	—	—	25·21	—	—	—
24	—	—	—	22·52	—	—	—
25	19681·27	19680·81*	—	19·78	—	61·26	—
26	80·85*	80·38*	—	16·97	—	63·64	66·91
27	80·38*	79·92*	—	14·13	--	66·02	69·37
28	79·88*	79·41*	19611·47*	—	19611·01	68·40	71·87
29	79·30*	78·83*	08·51*	—	08·05	70·78	74·40
30	78·68*	78·17*	05·47*	—	05·01	73·18	76·93
31	77·94*	77·44	02·36*	—	01·90	75·56	79·46
32	77·13	76·62	599·21*	—	598·71*	77·91	81·96
33	76·28	75·73	95·98	—	95·48*	80·27	84·44
34	75·35	74·81	92·68	—	92·18*	82·65	86·95
35	74·34	73·80	89·30	—	88·80*	85·02	89·47
36	73·30	72·7	85·88	—	85·35*	87·41	91·95
37	72·21	71·63	82·39*	—	81·86*	89·80	94·46
38	71·05	70·47	78·83*	—	78·29	92·20	96·97
39	69·81	69·23	75·22*	—	74·69	94·57	99·47
40	68·53	67·95	71·58*	—	71·01	96·95	101·95
41	67·22	66·60	67·86	—	67·29*	99·34	104·45
42	65·79	65·17	64·08	—	63·50*	101·69	106·97
43	64·32	63·70	60·25	—	59·64	104·07	109·45
44	62.77*	62·11	56·34	—	55·73	106·41	111·95

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TABLE I (*contd.*)

(0, 1) Band.(*contd.*)

K″	R₁	R₂	P₁	P₂	Δ₂T′	Δ₁T‴
45	19661·15*	19660·49	19552·37	19551·75	108·76	114·40
46	59·45*	58·79	48·35	47·74	111·08	116·85
47	57·70	57·05	44·30	43·65	113·40	119·27
48	55·89	55·19	40·18	39·53	115·69	121·72
49	54·00	53·30	35·98	35·33	118·00	124·17
50	52·06	51·37	31·70	31·05	120·34	12·63
51	50·05	49·36	27·35	26·70	122·68	129·09
52	48·01	47·27	22·97	22·28	125·02	131·54
53	45·89	45·15	18·51	17·82	127·36	134·01
54	43·68	42·95	13·97	13·29	129·68	136·50
55	41·41	40·67	09·36	08·68	132·02	138·95
56	39·09	38.32	04·72	04·00	134·34	141·40
57	36·70	35·93	00·00	499·28	136·67	143·81
58	34·27	33·50	495·25	94·53	138·99	146·21
59	31·76	30·99	90·46	89·74	141·27	148·64
60	29·18	28·37	85·60	84·88	143·53	151·09
61	26·52	25·71	80·66	79·90	145·83	153·54
62	23·79	22·98	75·61	74·86	148·15	156·00
63	21·01	20·20	70·49	69·74	150·49	158·44
64	18·17	17·32	65·34	64·54	152·80	160·89
65	15·24	14·40	60·11	59·31	155·11	163·30
66	12·28	11·43*	54·84	54·05	157·41	165·68
67	09·28	08·40*	49·54	48·75	159·70	168·06
68	06·20	05·32*	44·21	48·38	161·97	170·45
69	03·05	02·17*	38·81	37·97⁻	164·22	172·85
70	599·82	598·90*	33·33	32·50	166·45	175·29
71	96·52	95·60*	27·74	26·91	168·74	177·69
72	93·14	92·22*	22·11	21·24	171·01	180·12

TABLE I (*contd.*)

(0, 1) Band (*contd.*)

K″	R₁	R₂	P₁	P₂	Δ₂T′	Δ₂T″
73	19589·72	19588·76*	19416·38	19415·51	173·30	182·54
74	86·19	85·23*	10·58	09·71	175·57	184·94
75	82·59*	81·62*	04·73	03·87	177·80	—
76	78·90*	77·91	—	—	—	—
77	75·14*	74·15	—	—	—	—
78	71·31*	70·32	—	—	—	—
79	67·43*	66·41	—	—	—	—
80	63·46*	62·43	—	—	—	—

(1, 2) Band.

K″	R₁	R₂	P₁	P₂	Δ₂T′	Δ₂T″
12	—	—	19562·77		—	—
13	—	—	60·86		—	—
14	—	—	58·87		—	—
15	—	—	56·80		—	—
16		—	54·62		—	—
17	—	—	52·40*		—	—
18	—	—	50·11		—	—
19	—	—	47·78*		—	—
20	—	—	45·37		—	—
21	—	—	42·85		—	—
22	—	—	40·25*		—	—
23	—	—	37·62		—	—
24	—	—	34·94		—	—
25	—	—	32·20		—	—
26		—	19529·64	19529·18	—	—
27	—	—	26·82*	26·36	—	—

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TABLE I (*contd.*).

(1, 2) Band (*contd*).

K″	R₁	R₂	P₁	P₂	Δ₂T′	Δ₂T″
28	19591·83	19591·26*	19523·96	19523·56	67·81	—
29	91·30*	90·72⁺	21·06	20·56	70·20	73·70
30	90·72*	90·15*	18·09*	17·59*	72·59	76·22
31	90·07*	89·49*	15·04	14·54	74·99	78·75
32	89·38*	88·76⁺	11·95	11·42	77·39	81·26
33	88·61*	88·00*	08·79*	08·26	79·78	83·74
34	87·76*	87·15	05·00	05·06	82·12	86·23
35	86·84	86·23*	02·36	01·79	84·46	88·69
36	85·88*	85·23*	499·05*	498·48	86·79	91·19
37	84·85	84·20	95·63	95·06	89·18	93·69
38	83·74	83·08	92·17	91·56	91·55	96·19
39	82·55*	81·89*	88·64	88·03	93·89	98·65
40	81·32	80·63	85·07*	84·46	96·21	101·09
41	80·01	79·32	81·46	80·81*	98·53	103·48
42	78·67*	77·98*	77·82	77·17	100·83	105·85
43	77·29	76·60	74·13	73·49	103·13	108·28
44	75·87	75·19*	70·38*	69·70*	105·49	110·73
45	74·42*	73·69	66·55	65·87	107·84	113·22
46	72·89	72·16	62·65	61·97	110·21	115·68
47	71·27*	70·55*	58·71	58·03	112·54	118·17
48	69·59	68·86	54·69*	54·01*	114·87	120·65
49	67·83*	67·10*	50·61	49·92	117·20	123·10
50	66·03	65·26	46·48	45·76	119·52	125·54
51	64·15*	63·39*	42·28	— 41·56	121·85	127·95
52	62·20*	61·43	38·05	37·33	124·12	130·39
53	60·17*	59·40*	33·74	33·02	126·40	132·79
54	58·10	57·30	29·40	28·64	128·68	—

TABLE II

$\Delta_2 T_1(K)$ and $\Delta_2 T_2(K)$ values for the upper $^2\Sigma$ state.

K	$v = 0$		$v = 1$		$v = 2$	
	$\Delta_2 T_1 (K)$	$\Delta_2 T_2 (K)$	$\Delta_2 T_1 (K)$	$\Delta_2 T_2 (K)$	$\Delta_2 T_1 (K)$	$\Delta_2 T_2 (K)$
24	58·92	58·86	...	...	...	...
25	61·27	61·19	...	...	...	...
26	63·65	63·56	63·25	63·18	62·77	62·72
27	66·05	65·97	65 57	65·51	65 12	65·08
28	68·44	68·39	67·90	67·83	67·49	67·44
29	70·83	70·78	70·26	70·20	69·84	69·79
30	73·22	73·15	72·64	72·57	72·15	72·05
31	75·59	75·52	75·00	74·95	74·46	74·36
32	77·94	77·89	77·37	77·31	76·76	76·71
33	80·31	80·26	79·74	79·68	79·11	79·07
34	82·69	82·65	82·08	82·03	81 46	81·37
35	85·08	85·01	84·45	84·39	83 76	83·67
36	87·46	87·41	86·82	86·75	86·11	86·02
37	89·86	89·79	89·17	89·10	88·50	88·40
38	92·24	92·17	91·51	91·46	90·84	90·79
39	94·59	94·52	93 86	93·81	93·18	93·09
40	96·94	96·89	96 21	96·12	95·47	95·37
41	99·32	99·25	98 55	98·47	97·76	97·66
42	101·67	101·60	100·89	100·83	100·05	99·95
43	104·02	103·96	103 21	103·16	102·34	102·28
44	106·39	106·31	105·53	105·50	104·71	104·65
45	108·75	108·68	107·88	107·81	107·08	106·99
46	111·09	111·02	110·24	110·15	109 36	109·25
47	113·43	113·38	112·57	112·49	111·67	111·59
48	115·75	115·66	114·92	114 85	113·95	113·00
49	118·06	117·98	117·23	117·18	116·26	116·22
50	120·40	120·33	119·54	119·49	118·59	118·52

TABLE II (*contd.*)

$\Delta_2'T_1(K)$ and $\Delta_2'T_2(K)$ values for the upper $^2\Sigma$ state.

K	$v = 0$		$v = 1$		$v = 2$	
	$\Delta_2'T_1(K)$	$\Delta_2'T_2(K)$	$\Delta_2'T_1(K)$	$\Delta_2'T_2(K)$	$\Delta_2'T_1(K)$	$\Delta_2'T_2(K)$
51	122·73	122·68	121·85	121·81	120·94	120·83
52	125·06	124·98	124·16	124·08	123·25	123·19
53	127·38	127·31	126·46	126·38	125·60	125·54
54	129·70	129·63	128·76	128·68	127·89	127·84
55	132·04	131·99	131·04	130·97	130·15	130·10
56	134·38	134·33	133·31	133·26	132·36	132·31
57	136·72	136·67	135·62	135·56	134·57	134·51
58	139·03	138·98	137·98	137·88	136·81	136·76
59	141·31	141·26	140·28	140·23	139·10	139·05
60	143·58	143·53	142·59	142·54	141·38	141·33
61	145·89	145·84	144·89	144·79	143·66	143·61
62	148·19	148·13	147·19	147·09	145·94	145·89
63	150·52	150·47	149·44	149·38	148·26	148·21
64	152·82	152·79	151·69	151·63	150·58	150·52
65	155·13	155·08	153·93	153·87	...	..
66	157·42	157·36	156·21	156·12	...	...
67	159·68	159·63	158·50	158·43	...	...
68	161·97	161·91	160·77	160·71	...	...
69	164·24	164·19	163·01	162·95	..	...
70	166·52	166·44	165·27	165·17	...	...
71	168·79	168·74	167·54	167·48	...	...
72	171·06	171·01	169·79	169·74	...	...
73	173·34	173·27	172·01	171·95	...	...
74	175·60	175·52	174·27	174·15	...	•••
75	177·84	177·76	176·52	176·40	...	...
76	180·05	180·01	178·76	178·70	...	...
77	182·30	182·23	181·01	180·94	...	...

TABLE II (*contd.*)

$\Delta_2T_1(K)$ and $\Delta_2T_2(K)$ values for the upper $^2\Sigma$ state

K	$v = 0$		$v = 1$		$v = 2$	
	$\Delta_2T_1(K)$	$\Delta_2T_2(K)$	$\Delta_2T_1(K)$	$\Delta_2T_2(K)$	$\Delta_2T_1(K)$	$\Delta_2T_2(K)$
78	184·52	184·46	183 24	183·13	...	...
79	186·70	186·69	185·42	185·31	...	...
80	188·96	188·90	187·57	...	...	...
81	191·23	191·16	189·79	...	...	...
82	193·53	193·46	192·01	...	...	...
83	195·77	195·71	...	...	...	...
84	197·98	197·92	...	...	..	...
85	200·14	200·08	...	...	...	...
86	202·29	202·23	...	...	...	...
87	204·44	204·44	...	...	...	...
88	206·62	206·56	...	...	...	...
89	208·81	208·75	...	...	...	...
90	211·03	210·96	..	...	...	...
91	213·24	213·18	...	...	...	...
92	215·45	215·39	...	...	...	...
93	217·62	217·55	...	...	..	.
94	219·77	219·71	...	..	...	..
95	221·93	221·86	...	..	...	..
96	224·16	224·05	..	...	.	...
97	226·30	226·20	...	..	...	...

TABLE III

$\Delta_2T_1(K)$ and $\Delta_2T_2(K)$ values for the lower $^2\Sigma$ state.

K	$v = 0$		$v = 1$		$v = 2$	
	$\Delta_2T_1(K)$	$\Delta_2T_2(K)$	$\Delta_2T_1(K)$	$\Delta_2T_2(K)$	$\Delta_2T_1(K)$	$\Delta_2T_2(K)$
25	65·02	64·97	...	...	...	...
26	67·54	67·50	...	...	...	...

TABLE III (*contd.*)

$\Delta_2T_1(K)$ and $\Delta_2T_2(K)$ values for the lower $^2\Sigma$ state

K	$v = 0$		$v = 1$		$v = 2$	
	$\Delta_2T_1(K)$	$\Delta_2T_2(K)$	$\Delta_2T_1(K)$	$\Delta_2T_2(K)$	$\Delta_2T_1(K)$	$\Delta_2T_2(K)$
27	70·10	70·05	69·54	69·49	...	...
28	72·63	72·56	72·02	71·98	...	..
29	75·15	75·10	74·47	74·43	73·74	73·67
30	77·67	77·63	76·95	76·93	76·26	76·18
31	80·22	80·15	79·44	79·42	78·77	78·73
32	82·74	82·69	81·95	81·93	81·28	81·23
33	85·26	85·21	84·46	84·42	83·78	83·70
34	87·78	87·73	86·96	86·91	86·25	86·21
35	90·31	90·27	89·45	89·42	88·71	88·67
36	92·85	92·77	91·95	91·91	91·21	91·17
37	95·36	95·28	94·45	94·41	93·71	93·67
38	97·87	97·80	96·93	96·88	96·21	96·17
39	100·38	100·32	99·41	99·37	98·67	98·62
40	102·88	102·83	101·91	101·86	101·09	101·08
41	105·40	105·31	104·41	104·36	103·50	103·46
42	107·91	107·83	106·90	106·86	105·88	105·83
43	110·40	110·35	109·37	109·34	108·29	108·28
44	112·90	112·84	111·86	111·89	110·74	110·73
45	115·41	115·34	114·32	114·27	113·22	113·22
46	117·94	117·85	116·81	116·76	115·71	115·66
47	120·45	120·35	119·29	119·25	118·20	118·15
48	122·94	122·86	121·77	121·74	120·66	120·63
49	125·40	125·32	124·24	124·18	− 123·11	123·10
50	127·85	127·80	126·69	126·64	125·55	125·54
51	130·33	130·27	129·14	129·13	127·98	127·93
52	132·83	132·77	131·60	131·57	130·41	130·37
53	135·32	135·21	134·07	134·01	132·80	132·79

TABLE III (*contd.*)

$\Delta_2 T_1(K)$ and $\Delta_2 T_2(K)$ values for the lower $^2\Sigma$ state.

K	$v = 0$		$v = 1$		$v = 2$	
	$\Delta_2 T_1(K)$	$\Delta_2 T_2(K)$	$\Delta_2 T_1(K)$	$\Delta_2 T_2(K)$	$\Delta_2 T_1(K)$	$\Delta_2 T_2(K)$
54	137·78	137·72	136·53	136·47	.	...
55	140·27	140·22	138·94	138·91	..	.
56	142·73	142·69	141·36	141·34	...	
57	145·19	145·16	143·78	143·76	...	..
58	147·66	147·63	146·22	146·17	...	.
59	150·11	150·08	148·67	148·61	.	...
60	152·58	152·55	151·11	151·08	..	...
61	155·05	155·02	153·57	153·52	...	..
62	157·51	157·45	156·03	156·00	...	...
63	159·92	159·89	158·46	158·46	...	...
64	162·36	162·32	160·90	160·89	...	...
65	164·81	164·78	163·33	163·27	...	..
66	167·26	167·24	165·70	165·65	...	...
67	169·70	169·67	168·07	168·05	...	..
68	172·13	172·08	170·47	170·43	...	...
69	174·56	174·50	172·87	172·82	...	..
70	176·97	176·95	175·31	175·26	...	..
71	179·40	179·36	177·71	177·66	...	...
72	181·82	181·79	180·14	180·09	...	...
73	184·26	184·20	182·56	182·51	...	..
74	186·64	186·59	184·99	184·89	...	...
75	189·05	189·01	...	...	...	...
76	191·48	191·41	...	...	...	...
77	193·88	193·82	...	.	...	...
78	196·26	196·22	..	...	...	..
79	198·63	198·59	...	...	...	...
80	201·00	200·95	...	...	...	..

Table III (contd.)

$\Delta_2 T_1(K)$ and $\Delta_2 T_2(K)$ values for the lower $^2\Sigma$ state.

	v = 0		v = 1		v = 2	
K	$\Delta_2 T_1(K)$	$\Delta_2 T_2(K)$	$\Delta_2 T_1(K)$	$\Delta_2 T_2(K)$	$\Delta_2 T_1(K)$	$\Delta_2 T_2(K)$
81	203·39	203·32	...	..	..	...
82	205·76	205·74	...	.	..	...
83	208·17	208·15	...		..	...
84	210·53	210·47	..	...	...	...
85	212·85	212·79	...	...	...	.
86	215·16	215·14	...	..	...	..
87	217·51	217·48	...	...	...	..
88	219·86	219·79	...	...	...	...
89	222·19	222·17	...	...	...	..
90	224·52	224·51	...	...	...	..
91	226·89	226·83	...	...	..	...
92	229·22	229·19	..	...	..	.
93	231·58	231·55	..	...	...	..
94	233·94	233·87	...	..	...	...
95	236·28	236·22	...	..	...	...
96	238·59	238·52	...	..	...	.

MOLECULAR CONSTANTS

The rotational constants, B_v and D_v and their variation with v were evaluated from the $\Delta_2 T(K)$ values given in table I. In cases where more than one such value was obtained for a particular pair of rotational levels, their mean was taken. It is well known that the combination differences calculated from the centres of R and P doublets of a band can be expressed in the form

$$\Delta_2 T(K) = 4B_v(K + \tfrac{1}{2}) + 8D_v(K + \tfrac{1}{2})(K^2 + K + 1) + \dots \qquad (16)$$

$$\left.\begin{array}{l} \text{where } B_v = B_e - a(v + \tfrac{1}{2}), \\[4pt] \text{and } D_v = D_e + \beta(v + \tfrac{1}{2}). \end{array}\right\} \qquad \dots \qquad (17)$$
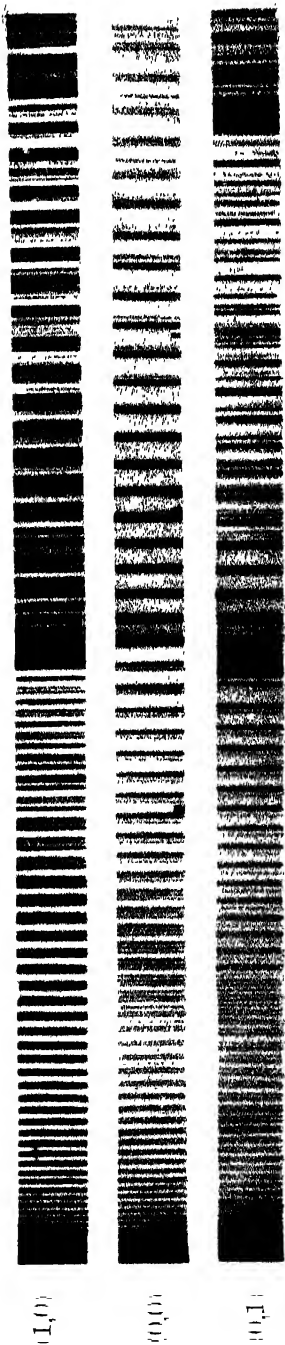
Figure 1.

By a method of successive approximation, the values B_v and D_v'' for different v values were estimated. They are given in table IV. Using these data, the calculated values of $\Delta_2 T(K)$ are mutually in good agreement with the observed data in each case. It is further found that the variation of B_v or of D_v with v is linear in conformity with equation (17).

From a knowledge of B_e, the values of I_e and r_e were evaluated on the basis of the following equations, viz.,

$$I_e = \frac{(27 \cdot 66 \pm 0 \cdot 04) \times 10^{-40}}{B_e} \text{ gm. cm.}^2 \quad \ldots \quad \ldots \quad (18)$$

$$\text{and} \quad r_e = \sqrt{\frac{I_e}{\mu}} \text{ cm.} \quad \ldots \quad \ldots \quad \ldots \quad (19)$$

where μ is the reduced mass of the molecule and is given by

$$\mu = 1 \cdot 649 \times 10^{-24} \frac{A_1 A_2}{A_1 + A_2} \text{ gms.,}$$

A_1 and A_2 being the atomic weights of the two atoms concerned.

TABLE IV
Rotational Constants.

v	Upper $^2\Sigma$ state.		Lower $^2\Sigma$ state.	
	B_v'	D_v'	B_v''	D_v''
0	0·60190 cm.$^{-1}$	$-1 \cdot 163 \times 10^{-6}$ cm.$^{-1}$	0·63860 cm.$^{-1}$	$-1 \cdot 1094 \times 10^{-6}$ cm.$^{-1}$
1	0·59737 ,,	$-1 \cdot 157 \times 10^{-6}$,,	0·63285 ,,	$-1 \cdot 1181 \times 10^{-6}$,,
2	0·59284 ,,	$-1 \cdot 1512 \times 10^{-6}$,,	0·62710 ,,	$-1 \cdot 1268 \times 10^{-6}$,,

$B_e' = 0 \cdot 60417$ cm.$^{-1}$; $D_e' = -1 \cdot 1660 \times 10^{-6}$ cm.$^{-1}$; $B_e'' = 0 \cdot 64148$ cm.$^{-1}$; $D_e'' = -1 \cdot 1050 \times 10^{-6}$ cm.$^{-1}$

$I_e' = 45 \cdot 85 \times 10^{-40}$ gm. cm.^{2}; $I_e'' = 43 \cdot 18 \times 10^{-40}$ gm. cm.^{2}

$r_e' = 1 \cdot 664 \times 10^{-8}$ cm. $r_e'' = 1 \cdot 615 \times 10^{-8}$ cm.

DISCUSSION OF RESULTS

Table V contains the mean γ-values in the two electronic states for different values of v. They have been evaluated by means of equation (11) from $\Delta_2 T_1 (K + \frac{1}{2})$ and $\Delta_2 T_2 (K - \frac{1}{2})$ values of bands having the same v'- or v''-value.

It is evident that since both γ' and γ'' are small in magnitude, the terms $\frac{1}{2}(\gamma' + \gamma'')$ and $\frac{1}{2}(3\gamma' - \gamma'')$ representing the magnitude of the intercepts of $\Delta\nu_{12}$ (P): K and $\Delta\nu_{12}$(R): K curves, although have finite values, would be indistinguishable from one another. Hence the two curves, which have the same gradient, would lie very close to one another. To a first approximation, a mean straight line can therefore be drawn for each band. This would pass through the

7

$\Delta \bar{v}_{12}$ (P): K AND $\Delta \bar{v}_{12}$ (R): K CURVE FOR (0,0) BAND
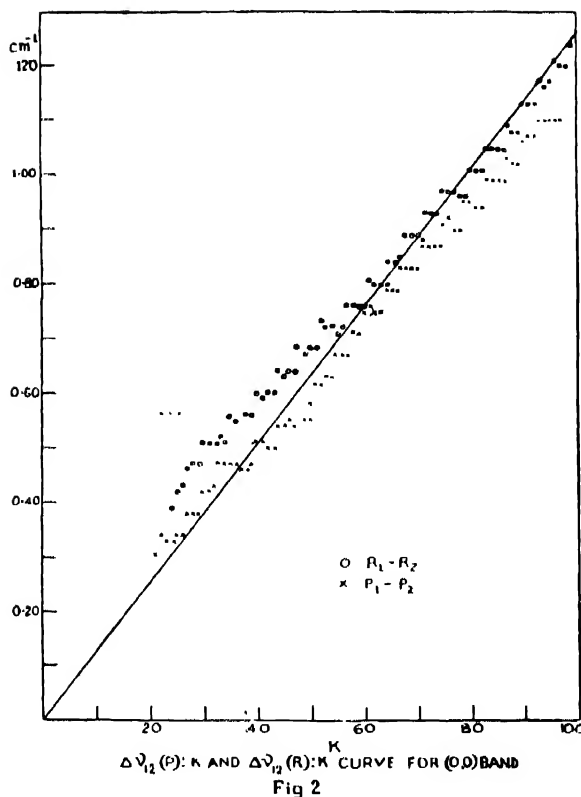
Fig 2

origin since the mean intercept $\gamma' - \gamma''/2$ is negligibly small. From the gradient of this mean curve, a mean value of $\gamma' - \gamma''$ can be estimated. Such values of $\gamma' - \gamma''$ for the different bands are also included in table V. In figure 2, a typical illustration of the nature of the mean curve in the case of (o, o) band is shown. It clearly shows that the width of the spin doublets is proportional to $(K + \frac{1}{2})$.

TABLE V

γ-values.

v	γ'	γ''
o	o'o3o3 cm.$^{-1}$	o'o211 cm^{-1}
I	o'o329 ,,	o'o197 ,,
2	o'o340 ,,	o'o162 ,,

$\gamma_0' - \gamma_0'' = $ o'o127 cm^{-1} $\gamma_1' - \gamma_1'' = $ o'o142 cm^{-1}

$\gamma_1' - \gamma_0'' = $ o'o139 $\gamma_2' - \gamma_1'' = $ o'o148

$\gamma_0' - \gamma_1'' = $ o'o130 $\gamma_1 - \gamma_2'' = $ o o158

From the values of γ' and γ'' given in Table V, it is easily seen that the spin doubling, although very small in magnitude, is present in both the upper and lower states of the band system. Furthermore it is noticed that γ increases with v in the upper $^2\Sigma$ state while it diminishes with v in the lower $^2\Sigma$ state.

It has been noted elsewhere that from the equality of the doublet widths in the (o, o) and (1, o) bands, Pomeroy had concluded that the spin doubling in the upper state is zero. This seems to be in contradiction with the present conclusion. It is evident from equation (13a) and (13b) that if $\Delta\nu_{12}(P):K$ and $\Delta\nu_{12}(R):K$ curves for any two bands coincide, it would simply show that they have γ' and γ'' values differing but little from one another with variation of v. It would not indicate that either of them is evidently zero. It is only when the interval between these curves for a given band vanishes that one can consider the spin doubling in the upper state to be zero. In the present case although one is tempted to make such a conclusion in view of the low value of the interval existing between the two curves, the agreement between the values of $\gamma'-\gamma''$ obtained from their gradients with those evaluated directly from γ' and γ'' values from the data of combination differences, $\Delta_2 T_1(K)$ and $\Delta_2 T_2(K)$, is too good to be left out of account.

The present conclusion is also in conformity with the idea that in the lowest $^2\Sigma$ state of a series of homologous molecules, as in the case of CaH, SrH, BaH as well as ZnH, CdH and HgH, the value of γ increases in magnitude as one passes from a lighter to a heavier molecule. In the case of the $^2\Sigma \longrightarrow {}^2\Sigma$ band system of BO, namely, the β-bands, $\gamma''=0$ and $\gamma' < 0.02$ cm.$^{-1}$ The value of γ'' and γ' given in table V are in the right direction for AlO. This shows further that in the emission of the two band systems under comparison, the corresponding states of the two homologous molecules are most likely involved. The only point against this view is that the band system under consideration does not occur in the region expected from an analogy with the β-system of BO and with the $^2\Sigma \longrightarrow {}^2\Sigma$ system of GaO recently reported.[7] Although such deviations are not rare, it is of interest to search for new band system of AlO.

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ON THE CRYSTAL STRUCTURE OF p-DICHLOROBENZENE AT DIFFERENT TEMPERATURES.

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AND

J. GUPTA.

Plate XI

ABSTRACT. Two Laue patterns of a single crystal of *p*-dichlorobenzene mounted with its 100 face approximately normal to the X-rays have been photographed, one with the crystal kept at a temperature just above 37°C and in the case of the other the crystal being cooled and kept below 20°C. The two Laue patterns are observed to be identical. No evidence is, therefore, obtained of the transformation from α to β-modification which Vuks has recently reported to have observed by raising the temperature of these crystals just above 32°C, while studying their Raman spectra.

It was first pointed out by Bech and Ebbinghaus [1] that when certain organic crystals are cooled below some critical temperatures, a sudden contraction of volume takes place. From this observation, they concluded that the contraction of volume is due to a change in the lattice of the crystals and that these crystals exist in two modifications, one above and the other below the critical temperature, called the β- and the α-modifications respectively. One of the substances exhibiting this phenomenon is *p*-dichlorobenzene. Recently, Vuks [2] studied the Raman spectra of the crystals of *p*-dichlorobenzene at different temperatures and observed that some of the new lines which appear in the case of the solid state in the neighbourhood of the Rayleigh line are shifted slightly with the transformation from α- to β-modification. He also reported to have grown a large single crystal by slow cooling of the melts and observed that the transformation mentioned by Bech and Ebbinghaus takes place at about 39°C, starting from the surface of the crystal. Later on. the present authors [3] studied the Raman spectra of this substance as well as of *p*-dibromobenzene at different temperatures including that of liquid oxygen. It was observed that though the transformation point of *p*-dichlorobenzene, according to Bech and Ebbinghaus is 39°C, the Raman spectra at 30°C and at 45°C are identical, but when the crystals are once immersed in ice-cold water and again brought to the room temperature (30°C), some of the new lines as well as some of the lines due to the intramolecular vibrations of the single molecule are slightly shifted. No such change was, however, observed in the case

of p-dibromobenzene, though these two substances are isomorphic with each other. These results led the present authors to the conclusion that the shift of the lines do not definitely lead to the conclusion that these lines are due to lattice oscillations. The observations which led to the above conclusion have since been confirmed by Vuks[4] who also has made a detailed investigation of the phenomenon and has also reported that the α-modification of p-dichlorobenzene is stable below 32°C and the β-modification above 32°C.

The question whether actually there are two modifications of the crystals under the conditions mentioned above could not be answered unequivocally from these observations, but it is only from the X-ray analysis of the crystals under proper conditions that definite information regarding the transformation can be obtained. The Debye-Scherrer and Laue patterns of the crystals have therefore, been studied at different temperatures and the results are reported in the present paper.

EXPERIMENTAL.

Since these crystals had already been investigated, it was first decided to study only the Debye-Scherrer patterns under different conditions of temperature. A cylindrical camera was used for this purpose. A few of the crystals of p-dichlorobenzene (Kahlbaum's pure variety) were melted in a test tube and a small quantity of the liquid mass allowed to solidify on a narrow tube of "Zigzag" paper mounted on the axle of the rotation apparatus. Three rotation diagrams of the polycrystalline mass were photographed, one at the room temperature (32°C), one at about 45°C and another at about 28°C after once cooling the crystals in ice-cold water. In the last case, the camera was cooled a little below room temperature with ice and was always kept at about 25°C during the exposure by keeping a few blocks of ice in contact with its lower portion. The substance in the paper-tube was cooled in ice-cold bath and was at once introduced into the camera without allowing it to attain the room temperature. As a slight change in the Raman spectrum was observed in this condition, special care was taken to obtain the Debye-Scherrer pattern under the same conditions. The pattern at 45°C was photographed by keeping the whole camera in an air bath at this temperature which was frequently measured during the exposure. Although the film (Agfa duplitized) was also heated in this crude arrangement, the film could be developed without any blackening effect due to heating being observed. A Shearer tube with copper anticathode and consuming a current of about 7 milliamperes was used with exposures for about 5 hours. Longer exposures could not be given, the crystals being volatile.

Only two fairly intense lines due to CuKα were observed, the values of 2θ being 52.°3 and 56.°3 respectively. It was found, after comparing with the results of a blank exposure with the paper tube only, that these two lines are

due to reflections from two planes in the crystal. The positions of these two lines were observed to remain unchanged in the Debye-Scherrer patterns obtained under the three different conditions mentioned above. These results indicated that probably there is only one modification of these crystals at the different temperatures, and it was thought worth while to investigate the Laue patterns of these crystals under similar conditions in order to confirm these conclusions more definitely.
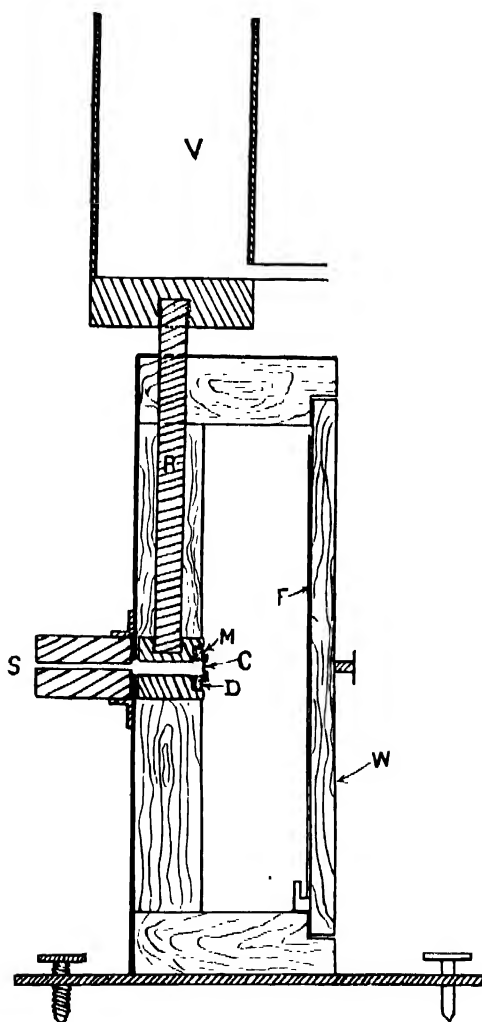
FIGURE 1.

A vertical section of the camera used for photographing the Laue patterns is shown in figure 1. The walls are of wood and lined outside with thick lead sheet. The slit S consists of a cylindrical hole along the axis of a lead cylinder about 3 cms. long. Just in front of this lead cylinder there is another copper cylinder T with an axial hole slightly wider than and co axial with that in the lead cylinder. The copper cylinder is provided with a groove on the front

surface in which a copper disc D fits almost tightly and is kept in position by two springs pressing against its edges. This disc also is provided with a cylindrical aperture along the axis slightly wider than and co-axial with that in the copper cylinder. The disc is again provided with a shelf having an aperture in front of that in the disc. A small strip of metal M about 5 mm. wide and 3/4 mm. thick could be slipped into this shelf. An aperture was cut in this piece of metal and the crystal C could be mounted therein. A copper rod R was inserted in a vertical hole in the wooden walls of the camera and was screwed to the copper cylinder T. The upper end of the rod was screwed into the bottom of a cylindrical copper vessel V provided with a side tube near the bottom. The vessel V was wrapped in thick woollen cloth. The temperature of the disc D could be raised to about 39°C−40°C by keeping water at about 58°C in the vessel V for some time. When blocks of ice were placed inside the vessel V, the temperature of the disc D came down within a short time to 17°C−18°C. The photographic film F could be mounted on the wooden plate W which could be taken out or put in its position without disturbing the camera.

A few single crystals in the form of plates about 4 sq. mm. in area and of thickness about 0˙5 to 0˙6 mm. were obtained from a bottle of Kahlbaum's para-dichlorobenzene. These crystals were also bounded by shining plane faces at one or two of the edges. The crystals are extremely volatile and a bare crystal could not be kept intact in its position in the camera for more than two hours. Two Laue patterns could not be photographed in two hours. No attempt was made to protect the crystal with a coating, because that might retard the transformation, if there were any. Hence the crystal, was finally mounted in a cell with windows made of " Zigzag " paper. This was done by covering first one side of the aperture in the metal strip M with the said paper, placing the crystal in position and then covering the other side also with the same paper. A small quantity of the substance placed inside the camera also retarded to some extent the sublimation of the single crystal. With the arrangements mentioned above, it was possible to expose the crystal to X-rays for about six hours and in this time two Laue patterns could be photographed.

As it has already been mentioned the shift of the new Raman lines can be observed only when the crystals are cooled much below the room temperature by placing them in a water bath cooled by ice. Hence at the room temperature (30°C) these crystals are ordinarily expected to exist in the β-modification. In order to further ensure this condition, a good single crystal about 0˙5 mm. thick was mounted in the copper disc in the way described above and the disc was introduced in a test tube which was then kept immersed in water bath at about 51°C for about half an hour. Meanwhile water heated to about 60°C was put in the vessel V of the camera and after the copper cylinder T became slightly warmer than the surrounding air, the warm copper disc was quickly removed from the glass tube and put in its position in the camera. The disc was held rigidly in
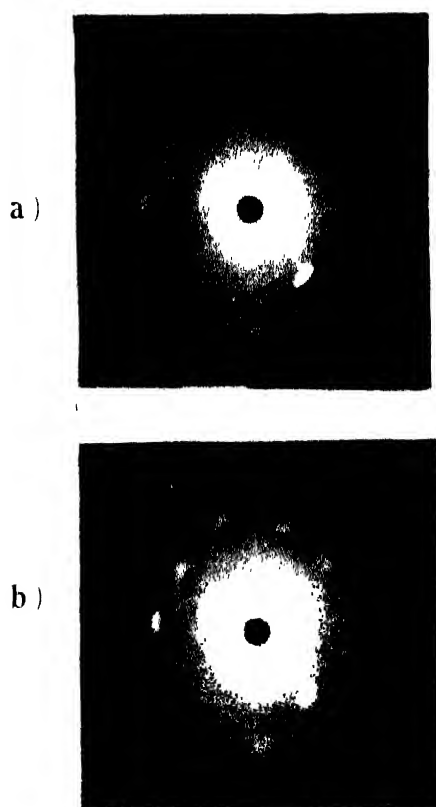
Laue Photographs of *p*-Dichlorobenzene

(*a*) at about 39°C
(*b*) ,,   ,,   18°C

.

its position by means of two springs and the metal strip M carrying the crystal was tightly fitted in the shelf so that the crystal could not be easily disturbed by any movement of the camera. The crystal was so mounted that its large faces were approximately normal to the X-rays. The photographic film wrapped in black paper was mounted in the wooden plate W which was then placed in its position in the camera. An exposure of about $2\frac{1}{2}$ hours was given with the X-rays from a Coolidge tube having a tungsten target the peak voltage applied being about 50 K.V. The water in the vessel V was allowed partly to run out through the side tube and fresh hot water was added every fifteen minutes. In this way the crystal was never allowed to cool down below about $37°C$ during the exposure. The film was taken out without disturbing the camera and developed. Next, without disturbing the crystal, it was cooled by keeping a block of ice in contact with the copper disc D for about ten to fifteen minutes, and meanwhile blocks of ice were placed also in the vessel V. The Laue pattern was photographed on another film with the same time of exposure as before. Blocks of ice were added into the vessel V frequently during the exposure. Thus two Laue patterns of the same crystal were photographed one with the crystal never coming below $37°C$ and the other at a temperature below $20°C$. This was repeated with four different crystals and identical results were obtained in all these cases.

RESULTS AND DISCUSSION.

The Laue patterns obtained with the hot and the cold crystal are reproduced in plate XI. It can be easily seen that the two patterns are almost identical. These crystals belong to the monoclinic prismatic class as has been confirmed by Hendricks [5] by X-ray analysis of these crystals. The face normal to the X-rays was the 100 face and therefore the b and c axes were in this plane. The direction of the c axis in the crystal can be easily identified because the crystal is elongated along this axis. Also the direction of the b axis can be easily identified in the Laue pattern because this axis is an axis of two-fold rotation. It was observed by examining the two patterns that the position of the b axis was the same in both the cases, i.e., when the warm crystal was cooled below $20°C$, the position of b axis in space remained unchanged. The other changes which could take place, if there were any transformation, were a change in the value of the angle β and a change in the axial lengths a and c. These changes however, would entail changes in orientation and the spacings of many of the planes and in that case, at least some of the Laue spots would have shifted considerably. Since they have not done so, it can be concluded that no such transformation takes place with the change of temperature. It may be mentioned here that a change of $1°$ in the direction of the normal to a plane hkl would produce a shift of about 1 mm. in the corresponding Laue spot in the case of some of the spots.

The structure may alter in another way ; the lattice remaining the same, the molecules may rotate to have new orientations in the unit cell. The only

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possible new structure obtained in this way would be identical with that of *p*-dibromobenzene. It has, however, been shown by Hendricks that with such a change in the structure, the relative intensities of reflections from many of the planes would alter so much that some of the intense spots would become feeble and some already feeble would become intense. Since no such change is observed in the Laue pattern reproduced in plate XI, it is doubtful whether such a change in structure actually takes place with the change of temperature. With such a change in structure, however, no change in volume is expected.

The original observations in which Bech and Ebbinghaus noticed a sudden contraction of the volume of the solidified melt with lowering of temperature below some critical temperature (39°C in this case) were repeated. Molten *p*-dichlorobenzene was gradually solidified in a thick test tube. The tube was next immersed in water at 30°C. It was observed that the whole mass near the inner surface of the test tube became transparent and its refractive index being nearly equal to that of glass, the surface of contact between the substance and glass walls could not be distinguished. Some portions of the substance round the axis of the tube, however, were opaque and therefore the whole mass looked detached from the walls of the tube, though actually it was not so. On immersing the tube in another water bath at about 39°·40°C, cracks developed at the surface of contact and the whole of the surface of contact became visible in a minute or two. Thus it is evident that there is no abnormal contraction of volume of the substance on cooling it below 39°C and the whole phenomenon is due to the equality of refractive indices of the substance and glass and also due to difference in the expansion of the glass and the crystals during sudden heating or cooling.

The above results that there is only one lattice in these crystals at different temperatures are significant in view of the fact that some changes take place in the positions of the Raman lines close to the Rayleigh line, when the crystals are once cooled below 20°C and brought back to 30°C again.

Some other organic crystals studied by Bech and Ebbinghaus will be examined with the help of X-rays shortly by the present authors.

The authors are indebted to Prof. D. M. Bose for his kind interest in the present work and for providing all the facilities for carrying out these investigations in the Palit Laboratory of Physics.

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INVESTIGATIONS ON THE RELEASE OF ELECTRICAL CHARGES UNDER MODERATE PRESSURE FROM PHOTOGRAPHIC PLATES AND OTHER MATERIALS.*

By Prof. K. PROSAD

AND

L. M. CHATTERJEE.

ABSTRACT.—An attempt has been made to study whether any electric charges are developed when moderate pressure is applied on a photographic plate or film, i.e., to see how far the ejection of electrons can serve as a physical basis for the pressure effect found. From the measurements recorded in the paper, it cannot be decisively asserted that there is an ejection of electrons when photographic plates or films are pressed moderately. Suggestions for future line of experiments to test more adequately the hypothesis have been made and it is hoped to undertake these measurements as soon as opportunity permits.

INTRODUCTORY

It is well known that agents other than radiation may leave their imprint on a photographic plate. Mechanical scratches as lines drawn by round point style are developable. M. Volmer[1] has described some experiments wherein an impression was made upon a photographic plate by drawing fine lines with rounded end of a glass rod. He referred to this as a pressure effect. Warnercke[2] seems to have been the first to note the effect of writing on a photographic film with a rounded glass rod using gentle pressure so as not to scratch the film; these marks developed out black. If, however, the plate was fogged with daylight before developing then the marks came out white on a dark back ground. This is the well known phenomenon of Photographic Reversal and an interesting account of it may be found elsewhere.[3, 4] The object of the present investigation was to study whether any electric charges are developed when moderate pressure is applied on a photographic plate, i. e., to see how far the ejection of electrons can serve as a physical basis for the pressure effect found, as was suggested by one of us in a recent paper.[4]

* Communicated by the Indian Physical Society.

PROCEDURE AND APPARATUS

As the photographic plate had to be protected from light, it was put inside a black paper envelope, the paper being previously well soaked in clean molten paraffin wax to make it insulator ; so during experiment, the composite system consisting of paraffined black paper, photoactive material spread over the thin glass plate and the glass itself was under pressure. To determine the effect of pressure on the photoactive material alone, we also tested the effect of pressure on the same glass plate, devoid of photoactive layer and put inside the paraffined black paper envelope. Alternatively, we also cut out two pieces from a photographic film, one of these was developed out without exposing to light and the remaining was left fresh. The two were placed side by side inside a paraffined black paper envelope. The pressure was first applied on one piece and then on the other. The difference, if any, in the electrical effects produced under pressure in the two pieces was attributable to AgBr alone.
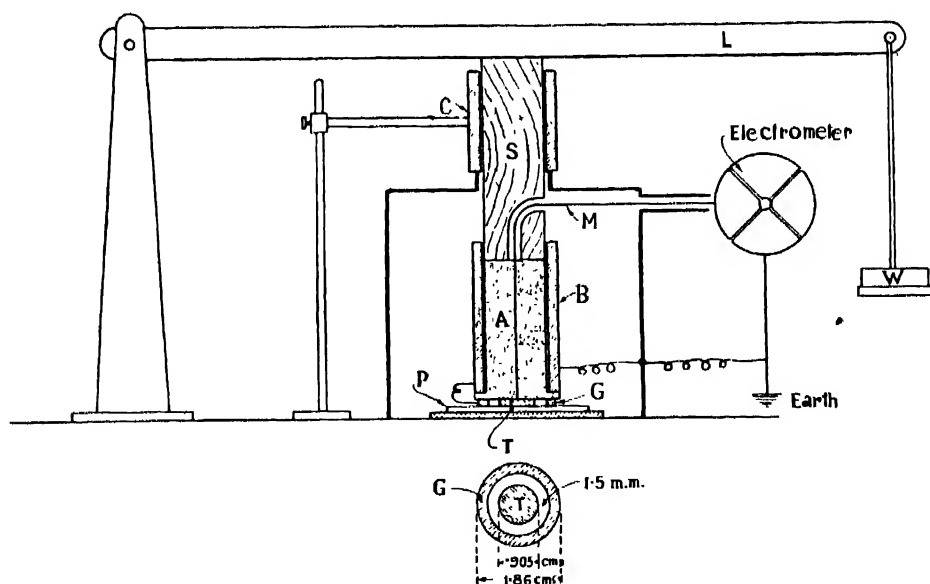
Details of test disc and guard ring.

FIGURE 1.

In figure 1, P is a photographic plate or film inside the envelope under test. The envelope lies on a stout brass plate at the bottom of an earthed metal box; the column standing vertically on P and being pressed by the lever L consists of (i) an amber rod A which is surrounded tightly by a hollow earthed brass cylinder B and (ii) a hard wooden rod S fitting closely into a groove at the top of the cylinder B, the lower end of S resting on A. C is a properly and rigidly clamped stout hollow brass cylinder acting as a guide to prevent lateral play of the press-

ing column. To the lower end of the amber pillar are fixed a circular brass disc T, 0˙64 sq. cm. in area and an earthed concentric guard-ring G flush with T. The clearance between the ring and the disc is about 1˙5 mm. A thin copper wire M connects the test disc T through a narrow bore in the amber rod and comes out of the pressing column sideways through a sufficiently wide ⌐-shaped boring in the wooden rod S, such that the wire does not touch any part of the wooden rod. The other end of this wire is connected to the insulated pair of the quadrants in a Dolezalek electrometer. Thus any charge received by the disc T fixed at the lower end of the pressing column and placed in contact with the envelope containing the photographic plate, will be indicated by the electrometer. A Wulf's single fibre electrometer was also employed as an alternative detecting instrument. If there be an ejection of electrons due to the pressure applied by the lever arrangement on the photographic plate or film, the surface of the plate will develop a negative charge at the localities pressed ; this will act inductively on the test disc accross the paraffined paper dielectric and the electrometer will indicate an acquisition of a negative charge. As the film is covered by an intervening layer of paraffined paper any charge released by pressure on the later will also simultaneously contribute to the indication of the electrometer. As we are considering either (*i*) the difference of electrical effect of pressure on a fresh film and that on a film developed without exposing to light—each under the same paraffined paper envelope or (*ii*) the difference of electrical effect of pressure on a fresh photographic glass-plate and that on the glass-plate from which the active layer has been removed—each, as before, enclosed within the envelope, so the charge released, if any, by pressing the envelope alone does not come into consideration.

RESULTS AND DISCUSSIONS

Maximum pressure applied was of the order of $3˙3 \times 10^{6}$ dynes per sq. cm. In general, a release of considerable amount of negative charge was shown by the
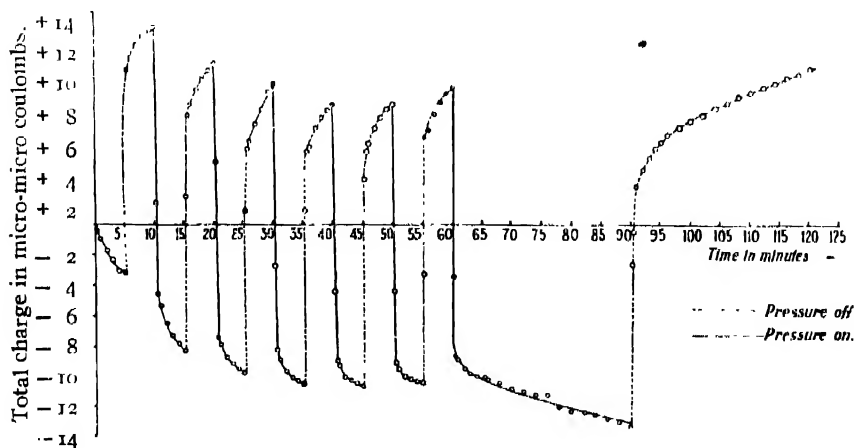
FIGURE 2.

electrometer when the system was pressed and a substantial decrease of this nega-
tive charge and sometimes a definite appearance of positive charge were observed
when the pressure was removed. Observations clearly illustrating the develop-
ment of positive charges whenever the pressure was released from a glass plate
under paraffined envelope are plotted in figure 2: but as the mechanism of this is not
very clear, discussion on the point is postponed for the present. Magnitudes of
these charges were different for different pressures and no regular relationship was
found to exist between them. In a series of observations with a particular pres-
sure, the observed charges differed appreciably and sometimes considerably from
one another as will be seen from the figures in table 1. A sudden substantial
decrease of negative potential indicated by the electrometer when the pressure is
removed cannot be accounted for by the assumption that there is a change in the
capacity of the system when pressed; because with a set of film and envelope the
capacity of the system with the test disc T loosely placed on the envelope and that
with the disc pressing were also measured; the difference was found to be too
small to account for the observed changes in charge, as is evident from the
actually measured values given below :—

Total capacity of the whole system including the quadrant electrometer and
the connecting wires.

Test plate loosely placed.

With a pressure of 2.12 × 10⁶ dynes on the
test plate.

61·56 e. s. u.

61·63 e. s. u.

TABLE 1.

No. of observations.	Negative charge indicated by the electro-meter in micro-micro-coulombs per sq. cm. of the surface pressed.		
	in case of fresh film under envelope.	in case of developed film under envelope.	in case of paraffined paper envelope alone.
1	13·68	9·58	9·58
2	6·84	4·10	10·94
3	5·47	13·68	5·47
4	12·31	8·21	8·21
5	6·84	6·84	5·47
6	10·94	5·47	12·31
7	6·84	10·94	8·21
8	5·47	6·84	10·94
9	13·68	13·68	8·21
10	9·58	10·94	9·58
Average	9·16	9·03	8·89

Thus the average negative charge released, when a fresh photographic film under envelope was pressed, was practically the same as that when a photographic film developed without exposing to light and placed inside the envelope was pressed. Also the average negative charge indicated by the electrometer when the pressure is applied on a photographic plate inside the envelope was found roughly the same as in the case of a glass plate alone put within the envelope, the photosensitive material being removed. From these measurements, therefore, it cannot be affirmatively and decisively asserted that there is an ejection of electrons when photographic films or plates are pressed moderately. But as pointed out later, further modifications in the experimental technique seem desirable before deciding the point.

In course of these experiments an interesting phenomenon was observed which is worthy of a detailed description. It was decided at first to ascertain what fraction of the total charge observed in the above-mentioned experiments was contributed by the compressed paraffined paper ; the investigation was repeated with a piece of paraffined paper alone and later on with a thin plate of paraffin wax. It was found that a considerable amount of negative charge, as indicated by the electrometer, was given out when these are pressed. These charges are solely due to the application of pressure. It is unlikely that any appreciable portion of the charge is due to friction. In the arrangement adopted every precaution was taken to eliminate sliding contact of the surfaces. The lateral play of the test disc 'T', if any, was exceedingly small and could not account for the magnitude of the charge actually developed. It was observed that when pressure is applied, the negative charge at first arises very suddenly and in large quantity and then slowly increases as the time goes on ; and the total negative
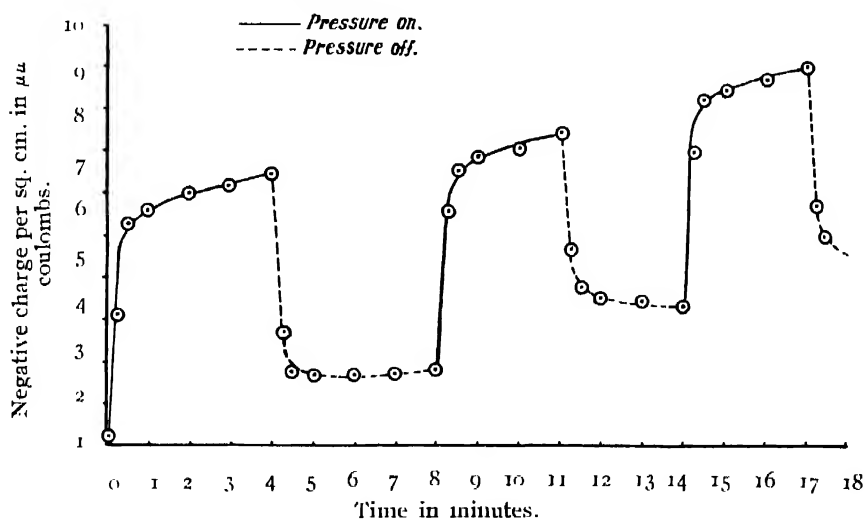
FIGURE 3.

charge released tends to approach a limiting value, as will be seen from the figure 3 which graphically represents how the quantity and the nature of the charge as

indicated by the electrometer connected to the test disc T vary as the pressure is successively applied and removed after interval of 3 or 4 minutes. It is certain that this squeezing out of the electrons cannot continue indefinitely, as the removal of the electrons from the crystallites and groups of molecules of the body under pressure will leave them positively charged which will tend to stop further movement of electrons towards the surface ; also a paraffined paper or a thin plate of paraffin wax first rapidly and then slowly and gradually yields to the applied pressure ; these facts explain the observed phenomenon that some time is elapsed before the maximum negative charge appears on the surface and the electrometer indication reaches an approximate saturation value in about 5 minutes and then very slowly creeps on. As the pressure is released the squeezed out electrons in the plate gradually recombines with the residual positively charged crystallites and groups of molecules left in the body. These electrons now go back to the interior and there is a marked decrease in the negative charge. It is not easy to explain the definite appearance of positive electrical charge which was actually the case on several occasions when pressure was removed. This may be due to some peculiar changes which take place when the compressed paraffined paper or a paraffin wax plate is relieved of pressure and gradually tends to settle down to its normal condition and is, to a certain extent, analogous to the piezo-electric phenomena found with quartz and a few other crystals, or it may be that electrons under released pressure overshoot their former equilibrium positions.

These experiments serve to indicate that the negative charge released by pressing the paraffined paper envelope is so large (see Table 1. last column) that it may altogether mask the little charge which might have been released by the application of pressure on a photographic plate put inside the envolpe. It could not be decisively settled that electrons are ejected when a photographic film or plate is pressed. It would be interesting to repeat the experiment in complete darkness without the use of the paraffined envelope and we hope to take up this work as soon as opportunity permits.

In conclusion, we should like to record our thanks to Mr. S. N. Chatterji for help in drawing the figures.

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SUPPLEMENTARY

THE MISSION OF THE PHYSICIST IN NATIONAL LIFE.

By PROF. M. N. SAHA, D.Sc., F.R.S. *

The Indian Physical Society is now passing through the third year of its existence and so far there has been no precedent compelling the president to deliver an address. When we consult the practice in similar societies in Europe and America, we find that there is no uniformity of practice. The German Physical Society with branches spread over all German-speaking countries does not compel its President to deliver any address ; neither do the French nor the American. In the Physical Society of London, the President, who holds office for two years, delivers one address during his tenure of office. I believe that in this respect, as in many others, it will be wise for us to follow the British practice.

The next point is choice of a subject. The President of the Physical Society of London generally delivers an address on some topic of current scientific interest. I think that the president of the Indian Physical Society should follow the same practice. But as you are probably aware, your President has been on tour throughout the major part of the past year, and he has not yet found time to sit down quietly and write out a purely scientific address. You will therefore excuse me if instead of delivering a purely scientific address, I entertain you to a kind of miscellany consisting of my experiences, as far as our subject is concerned, which I have gained in course of my travels, and of the future of our Profession in this country.

IN THE ROYAL INSTITUTION.

I will begin by recounting my experience which I obtained in course of a recent visit to the Royal Institution of Great Britain ; the present director, Sir William Bragg, President of the Royal Society, was kind enough to guide me personally through the scientific exhibits—reminiscent of the scientific works of his predecessors—Davy, Faraday, Tyndal and Dewar, and also of the earlier work of Count Rumford, the founder of the Royal Institution. Here I saw, not without a certain amount of thrill, some of the material used in the famous experiments which are now familiar wherever physics is read and practised : the famous ring of iron with copper wire which formed Faraday's first dynamo ; the heavy bent glass tube with a yellow

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* Presidential address delivered at the Third Annual General Meeting of the Indian Physical Society, held at Hyderabad-Deccan, on the 6th January, 1937.

liquid in one arm ; which I recognised as the apparatus in which Faraday lique-fied chlorine by the combined application of pressure and low temperature,—the little kerosene lamp (Davy's safety lamp) with the wire-gauze mantle about it which made mining safe, and a large number of others of which you may read a full account in the graphic description given by Sir William Bragg in his introduc-tion to Julian Huxley's charming book ' On Social Needs and Scientific Research.' But what struck me most was the idea with which the Royal Institu-tion was started. Probably very few of you will be prepared to believe that it started as a ' Society for improving the condition and adding to the comforts of the Poor ' by Count Rumford and a few other kindred spirits. To understand the significance of the new idea, we should remember that up to this time, philanthropic work was the monopoly of religious institutions alone, who set to do their task by giving doles to the poor or opening relief work for them. But this was not the way which Rumford proposed to follow in his self-imposed mission. He foresaw that Science had made possible a new kind of philanthropy, and if the knowledge of science were utilized to the common needs of mankind, great economy could be effected, and the poor would get relief against hunger, disease and weather at a cost which would be within the reach of everybody. Let us see how he proceeded in his work. A single example will show.

From his scientific studies, Rumford found that fire-places, boilers and cooking appliances in those days were very badly designed, and consumed a very large amount of coal. He designed new types of fire-places, boilers and cooking pots in which the consumption of coal was very substantially reduced so that poor people might cook their food at much reduced expense, would have not to inhale unhealthy fumes, and could get sufficient warmth and comfort.• Through some of his friends who were connected with big hospitals, he tried to introduce these new appliances amongst the public. But did he succeed ?

Sir William Bragg has a pathetic story to tell us. When these improved kitchens, and heating arrangements, the principles of which are now incorporated in all modern housing establishments, were introduced in some hospitals, they could not be made to work owing to the hostility of the cook who had the perqui-site of the dripping and her husband who had the perquisite of the cinders. What a lesson for all times !

Now to come to my point,—the basic idea with which Rumford started was that all human needs can be met and human distress relieved by systematic and judicious use of scientific knowledge. This is more true in these days than in former times on account of the wonderful progress science has made in all directions. If in any country medieval conditions still prevail, you can always presume that there is always some stupid orthodoxy, or entrenched Greed to oppose these humane schemes. This is nowhere more true than in this un-fortunate land of ours !

We cannot claim that application of the knowledge which a study of our subject has given to the world has always been attended with humane motives. Most frequently, the impulse has come from the motive of greater profits to the inventor. But nobody can deny that the application of such knowledge has entirely transformed the modes of living in the world during the last hundred and thirty years and has incidentally brought greater comfort to the poor and the needy. Whether the changes have been humane or not, there is no doubt that they have transformed all arts and crafts, and the modes of human life in Europe, America and Japan. Says Prof. K. T. Compton :—

" Historically we note that the Science of Physics has given birth nearly to all those ideas, processes and agencies which have brought man to an understanding of the Material Universe, and to the use of its forces, Civil Engineering, a large part of Chemical Engineering, Metallurgy, Electrical Communication, Refrigeration, Testing, Ventilating, Automotive, and Aeronautical and the countless products of those arts which have revolutionised modern life, not only in its material aspects, but also in intellectual, economic and social relationships. Physics has not only originated these things, but continues to develop them."

As a matter of fact a science which is playing such a great part in the evolution of human civilisation has certainly a great claim on Society and Governments. The material prosperity, and political safety of countries are intimately connected with the active cultivation of our Science.

It is therefore natural that in Europe, America, and Japan, increasing attention should be paid to the teaching of our subject in elementary and advanced schools, in professional schools, in the universities and technical high schools, in special research institutions maintained by the Government, private benefactions, or by the great industries which have sprung up as a result of the discoveries made in physics. Large amounts are willingly spent on research by Governments and Research Foundations. In England, the country which we follow, the change in the official attitude and the attitude of industrialists towards research since the Great War has been remarkable. Sir J. J. Thomson records in his personal recollections that in his days he had great difficulty in getting money for a little extension to the overcrowded Cavendish Laboratory and he had to do it by accumulating little savings for a number of years from the recurring laboratory grant. But largely as a result of the lessons learnt during the Great War, the attitude has been completely changed. Not only are the University laboratories far better equipped, but the number of research fellowships have increased enormously. You have all heard of the magnificent gift of Sir H. Austin to the Cavendish Laboratory, and of Lord Nuffield to the Oxford University, part of which will be spent on the improvement of the Clarendon Laboratory. Further, the department of Industrial and Scientific research spends about 1·30 million pounds in giving small doles to research workers, and a large number of them

are workers in physics. The Royal Society of London has been getting endowments for founding research professorships, and only a week ago, they were recipients of a magnificent sum of two million pounds. It is calculated by J. Huxley that the Industries in England spend about 5 to 6 million pounds in scientific research, and in the United States of America about 300 million dollars are annually spent in scientific research by Industries alone. A large part of this sum naturally goes to researches in pure physics or to researches in associated subjects. As a result of these endowments I found very few students of physics unemployed ; for the intellectually-minded it is quite easy to get research fellowships which enable them to keep the wolf out of doors while they are struggling with a fundamental problem. For those who have a mechanical and commercial bent of mind, there are hundreds of industrial concerns willing to profit by modern discoveries. What a sad contrast to the medieval conditions prevailing in this country !

UNEMPLOYMENT AMONGST PHYSICISTS IN INDIA.

The conditions prevailing in Europe, America and Japan with respect to the cultivation of the physical sciences and the place of the physicist in national life may be contrasted with those prevailing in this country. It is not many years that Physics found a place in the curricula of University and elementary education which is compatible with its importance. In fact, serious study of physics in the Indian Universities was first taken up only after the University reforms of 1904. Since this time, however, physical laboratories have been added almost to every university and college, and the schools are also gradually taking up the subject. A few of the University laboratories have grown into active research centres, and Indian Physicists have within a short time made original contributions to their subject the value of which is recognised in the world of international science. In spite of such auspicious beginning, it is feared that cultivation of the subject has not taken root in the soil of the country, which alone can ensure its vigorous growth in future. Every senior teacher in Physics knows how difficult it is for their meritorious students to get a footing in life ! It is a common experience that many young physicists who have proved their worth by making lasting contributions to the subject, have to wait for years before they can get a position in life, and many have not succeeded in getting any post at all ! It is the duty of the Indian Physical Society to analyse the causes of unemployment amongst the younger physicists, and devise methods for its cure, otherwise our science has no future in this country.

The causes of unemployment are not far to seek. The number of posts available for a trained physicist in India is very small compared to those available for chemists. It is largely because industries which absorb a large number of trained physicists have not developed in this country. Let us see how prospects in these directions can be improved.

Physicists in the Teaching Professions.

The largest number of physicists is to be found in the educational lines as professors of various grades in Universities, Colleges, Engineering Institutions, and as teachers in schools. Unfortunately, the number of University teachers in Physics is generally very insufficient, and has not kept pace with the rapid growth of the subject. In every European and American University, the number has almost doubled within the last ten years. One particular feature is the creation of posts of " Theoretical Physicists " in every University, as it has been felt that very few physicists can now handle competently both the theoretical and experimental sides of our subject. This practice should be followed in India by the creation of posts of theoretical physicists in every University, Intermediate Colleges, and Engineering Colleges.

Need of Refresher Course for Science Masters.

Under the new conditions which have been in vogue since 1923, between teachers of physics in intermediate and Engineering Colleges and those in the Universities, almost a Chinese wall of separation has been created. It is almost impossible for one who has distinguished himself in research work to get an employment in any intermediate College, for the authorities with whom decision rests have developed an obsession that those who have made a name in research work are unfit for teaching work in the schools and colleges. In England, on the contrary, I found the opposite opinion to prevail. Nobody is considered competent to teach even in a school or in a junior college unless he has some research training. In Scandinavian countries, I found that University teachers and science masters in what we call Intermediate Colleges are all State employees ; and by a very useful arrangement, science masters are enabled to take leave after three years, for a period not exceeding one year, which time they utilize in taking a full course in research, and qualifying for the doctorate degree in one, two or more turns. Science masters who have thus qualified themselves are allowed to compete for university posts, and I found that many prominent Scandinavian men in Science have risen from the ranks of Science masters. I think that some such practice may be followed in our country, so that science masters in schools and teachers in Intermediate Colleges may be enabled to come to the University to do some research work under competent professors. When some of them have shown aptitude in such work they should be allowed to qualify for their doctor's degree. Encouragement should be given in the way of better prospects and promotions to enterprising science masters, who have shown aptitude in research.

The effect of such an arrangement would be a much greater efficiency in the standard attained by science teachers in the Schools and Intermediate Colleges who under the present conditions find it very difficult to keep in touch with the rapid progress made in our subjects, and it is our experience that after a number of years they lose all interest in their subject

As an example of the evil effects of the present system I may cite the example of a Professor of Physics in a junior college in this country whom I met in 1911. He had never heard of the electron, because it had not been discovered when he took his M. A. degree in 1891. Even amongst my own students who have become professors in junior colleges after a good career, I have found, after such people have remained in the country for a number of years, they reveal appalling ignorance of all modern developments. I need hardly add that it is unsafe to place young boys in such hands, and the only remedy is to arrange for refresher courses in the way suggested above.

EMPLOYMENT OF PHYSICISTS IN HOSPITALS AND MEDICAL INSTITUTIONS.

It is usual for medical colleges to employ a teacher in Physics for giving junior medical students elementary lessons in physics. But there is now greater need for employment of Physicists trained in research in medical institutions and hospitals. Most hospitals are now provided with X-ray sets, and with Radium. In this country, it is the practice for medical authorities to train a medical man in the use of these apparatus according to the rule of thumb method. Whenever any difficulty occurs in the management of the apparatus. they usually call an expert engineer from outside to help them.

It is superfluous to add that such a practice is not only harmful but inefficient and expensive in the long run. In European countries the government maintain a number of trained physicists for the service of hospitals. Their duty is to keep the X-ray plants in order, assist the medical men with expert advice about the handling of apparatus and carry out researches on the standardisation of the doses to be applied. They sometimes conduct researches bearing on medical subjects in collaboration with medical men. Many hospitals in our country have now large quantities of Radium which are kept in small quantities distributed in a number of tubes As Prof. D. M. Bose pointed out sometime ago, this practice limits the utility of radium and is sometimes very ineffective. Radium should be kept under the charge of a trained physicist in a safe place in the hospital and the emanation evolved should be collected and stored in small tubes and given to medical men, official as well as non-official, on payment of small charges. Needless to say that this is the practice in all foreign countries.

There are indications that in future the latest advancements in physics will be more and more used for the investigation of fundamental medical and biological problems. During the Harvard tercentenary, I listened to a very interesting lecture by Prof. A. Krogh of the University of Copenhagen who in collaboration with Profs. Niels Bohr and Von Hevesy, is developing a fine technique based on the use of heavy hydrogen and radioactive isotopes of light elements for the study of fundamental physiological problems. As you are aware, it is possible now to obtain radioactive varieties of light elements like Na, Mg, which occur in our foodstuff and can be administered internally. In contradistinction to the ordinary varieties of these elements which, when taken as food or medicine undergo such chemical transformation within the human system as to render their identification impossible, the radioactive varieties each carry a special label, in the form of their ability to emit electrons or positrons with a certain life period, which render the course of diffusion of these elements through the system extremely easy of detection. Krogh, Madam Curie-Joliot and others have pointed out the extreme utility of this new technique for biological investigations and in course of my travel, I found that many great centres of research are equipping themselves with the latest appliances for producing artificial radioactivity in common elements. Thus physics which has so long been accused of dealing only with lifeless matter is placing at the disposal of medical science a fine technique for investigation of biological problems. I see a time when medical hospitals will be provided with cyclotrons for the production of light radioactive elements, and their administration to the human system. These arrangements will require the services of trained research workers in nuclear physics.

ALL-INDIA RADIO SERVICE.

The avenues of employment for the trained physicist have enormously increased in Western countries as a result of the opening of broadcasting services and television. Quite a large number of trained physicists are also absorbed as ordinary officials in charge of broadcasting stations, in factories manufacturing wireless goods and also in the research sections of factories and broadcasting services. A large number of men with very ordinary knowledge of physics are absorbed as wireless operators in ships, in the army and the navy. The system of recruitment for these services in this country are such that they practically favour only one community. It is almost impossible for Indian students to get employment in these services.

In recent years, a Broadcasting Service has been opened in India under the name " All-India Radio," with headquarters at Delhi. In this connection the following comparative figures may be of some interest : The United Kingdom with a population of 50 millions, has issued seven millions receiving licenses, *i.e.*,

one man in seven in the United Kingdom has a receiving set. In India the total number of receivers is only 38,000, *i.e.*, one man in 10,000 has a receiver. The objection may justly be raised that in the above comparison we have not taken into account the comparative poverty of India. This may be arrived at from the fact that the consumption of electricity per capita is only 6 units in India, while in England it is 420 units, *i.e.*, the average Englishman is 70 times richer than the Indian. On this basis one man in 500 in India ought to possess a receiver. The figures are twenty times lower. This shows that the management of the All-India Radio leaves much to be desired.

I have gone carefully into the cause of this inefficiency, and have elsewhere pointed how matters can be improved. All broadcasting organisations must have three well-organised sections—the technical section, the programme section, and the research section. The duty of the technical section is to construct transmitting stations, look after their running and maintenance. The work of this section can be carried on only by a competent technical staff who should have a thorough grasp of the fundamentals of the science, and should have opportunities of receiving practical training. It is well known that the Government has taken no steps to train a technical staff in India nor have utilized the available human material (which exists in plenty) in the country for this purpose. They depend entirely upon the foreign companies for helping them in this matter, and I am told that calls are frequently made upon foreign experts for setting apparatus right.

I do not wish to talk about the programme section which has received sufficient attention in the public press. The research section in a Broadcasting Organisation is as important as the two other sections, as a good deal of pains-taking work is needed before the proper site for a transmitting station can be found ; also for finding out the right conditions for short and long distance transmission, the causes of fade-outs, and signal strength measurements. Such research cannot be conducted by the technical staff of a government department but can only be carried out by a Radio Research Board consisting of University Professors, representatives of Post and Telegraph, and of manufacturing concerns and other parties interested in the development of Radio. This is the practice followed in all European countries, in America and in Japan.

Early last year the Government invited Mr. Kirke, the head of the research department of the British Broadcasting Corporation, to report on the steps to be taken for the development of radio in India. Though it is now over eight months that Mr. Kirke submitted his report, it has not yet seen the light of the day. I understand on reliable authority that many of the useful suggestions put forward by Mr. Kirke are being shelved by the Government of India.

Though some of the Indian Universities have done fundamental research work in the propagation of radio waves, the Government has never asked for their co-operation, and has never encouraged them either by giving

grants for research or by absorbing their students who have received special training.

The authorities in India are apparently of opinion that all the necessary research on radio problem in India could be very well undertaken by the newly formed research section of the All-India Radio : its organ, *Indian Listener*, in an editorial, gave expression to the same view. In a letter to the Editor (*Indian Listener*, Aug. 7, 1936), I pointed out several reasons why the research of the A. I. R. cannot perform the functions of a national radio research board.

" In the first place, the research section will be more concerned with immediate engineering problems of a commercial nature, and will not be able to undertake investigation of problems of a fundamental character, which is one of the main items in the programme of work of the Radio Research Boards. This is because the academic atmosphere which is necessary for the study of such problems is entirely wanting in the research section of a broadcasting organization.

Secondly, it has been our sad experience in the past that when a Government Department takes upon itself the task of carrying on fundamental research work, the duties of the officer engaged for the purpose very often begin and end in going through an interminable series of official files and the officer is hardly allowed any time for quiet thinking and sustained work ; the desire of the Government to carry out such investigations ultimately reduces to mere pious hope.

Thirdly, it has not been found possible for the research sections of other and much bigger broadcasting concerns to take upon themselves the performance of functions of Radio Research Boards, and it will no more be so for the newly formed similar section of the A.I.R.

(It may not generally be known that the British Broadcasting Corporation has a research section of which Mr. Kirke is the head. It deals with problems arising out of the technical development of the engineering of broadcasting and it has neither been within its scope, nor has it ever been its aim, nor indeed is it possible for it to perform the functions of the Radio Research Board.)"

OTHER AVENUES OF EMPLOYMENT FOR THE TRAINED PHYSICISTS.

Besides these departments, services of physicists are largely required for the Meteorological Survey of India. It is a rapidly expanding department and on account of its importance not only with respect to civil life, but also for the increasing demands of aerial transport, it should employ more physicists in future. The Geodetic Survey of India employs a few physicists, but the number may be considerably increased when a department of geophysics, including seismology and terrestrial magnetism, were added to it. The recent earthquakes in different parts of India have aroused the people to the importance of the fact that the

subject of earthquakes should be scientifically studied. It is understood that some time ago the Government of India appointed a Committee consisting of different heads of scientific services to go into this question. They gave a very detailed plan of installing seismographs in about 40 centres distributed all over India and in representative regions. Every one of these stations was to be managed by physicists whose duty would be to keep the instruments going, collect seismographs and try to find out the causes of earthquakes. In addition, there was to be a central seismological laboratory where researches on the possibility of prediction of earthquakes on the safety of buildings and other related phenomenon were to be investigated. We understand however that this very useful and sensible proposal has been turned down by the Government on the inevitable financial grounds.

RIVER PHYSICS LABORATORIES.

It is also hoped that in future the Government would see the wisdom of having a number of river physics laboratories in different regions of India. The importance of such a laboratory for the building up of the country cannot be overestimated. India is a land of big rivers and from time immemorial, human life has concentrated in the valleys of the great rivers, the Indus, the Ganges and the Brahmaputra and the South Indian rivers, the Godavari, the Krishna and the Kaveri. All the great centres of civilisation during the last 5,000 years have flourished on the banks of these rivers. But the rivers are liable to change their course and if they are not properly trained, not only do they cause floods and erosions, but the topography may be changed to such an extent as to give rise to unhealthy swamps and to malaria. The fate of the old centres of civilisation like Pataliputra and Gaur which now lie buried under the soil illustrates the effect of rivers, and very much the same fate is overtaking Calcutta under our very nose. In order to prevent these, it is necessary that the physics of the rivers should be properly studied in suitably designed laboratories. Research in this direction should be classified under several heads :—(1) Fundamental Research— which will deal more or less with theoretical problems like the hydrodynamic laws regarding the flow of rivers, deposit of silt, problems of erosion and so forth. (2) Then will come the field survey—which will deal with the actual discharge of the different rivers in India, their liability to changes and the best ways in which these changes can be controlled and the rivers may be trained so that most efficient measures for sanitation, navigation and for the purposes of irrigation may be devised. Unfortunately, though in the past engineering enterprises on a stupendous scale have been undertaken in India, interfering with the discharge and course of rivers, *e.g.*, by the throwing of bridges over the rivers, cutting of canals, these works have been done more or less haphazardly on insufficient knowledge and their bad effects have been felt only years after their

construction. It is high time that this department should be reorganised on a proper basis. If a number of river physics laboratories were opened as advocated here, they would give employment to a large number of physicists.

PHYSICS IN THE SERVICE OF INDUSTRY.

It is not realised what a large field exists for the application of physics to the problems of resuscitation of industrial life in the country. India is still an agricultural country and nearly 85 per cent. of her population live by agriculture. This disproportionate relation between agriculture and industry is not a healthy sign. The industries must be revived and put on a proper basis otherwise the standard of life in this country cannot be improved. The backwardness of India in industrial matters can be gauged from the following fact. For improvement of industries, the supply of power is an essential condition. In the most advanced industrial countries of the world, the supply of power is measured in the number of units of electricity consumed per head of the population in the year. In countries like Canada and Norway the consumption of electricity per capita amounts to about 2,000 units. In countries like Germany and England, a large amount of power is provided by steam, but even then the electrical power amounts to about 600 to 700 units per head. In India, the corresponding figure is only 6 per head. This shows how backward India is in matters of power supply.

It might be argued that this backwardness is the result of non-existence of power resources in this country. This is not a fact. Sir M. Visheshwaraya, ex-Dewan of Mysore, has estimated that the total power resources from hydro-electric sources alone amount to about 12 million kilowatts and of this barely 3 per cent. has been developed. If about 80 per cent. of the total power resources were developed the consumption of electricity per head in India would come to about 240 units. This would give India the same standard of living as in Japan and would provide her with a proportionate amount of power for the development of her industries. But there is neither the will nor a settled programme on the part of the Government of this country to undertake this electrification scheme.

Some people argue that industrial work like electrification should be left to private enterprises. Nothing can be farther from actual facts. In all European countries, in America and in Japan, the organisation of power resources of the country has been nationalised. It is never left to any private concern. Unfortunately in India, the electrical supply companies are all private bodies and as I have shown elsewhere they are all concerns for private profit. The result is that the price of power in this country is about 5 to 6 times higher than in other countries. On account of this high rate for power, industries cannot be developed to the same extent as in Europe and America. Unless this problem is seriously tackled, we shall always be at a disadvantage. Sooner or later the Government

will have to take up the problem of supplying the country with cheap electrical power. In a scheme like this the services of the physicists would be required not only for designing the power plant but also for running power stations, and for solving such problems as that of surge, leakage, proper insulation and distribution.

DEPARTMENT OF INDUSTRIAL AND SCIENTIFIC RESEARCH.

Mr. V. Gordon Childe in his book " Man makes himself " has given a very thoughtful review of the modern currents in human civilisation. According to him the present-day scientific inventions are ushering a new phase of human civilisation which he calls the Third Great Revolution. The first revolution was brought about by the invention of agriculture which enabled men to live in settled cities and develop a sedentary civilisation. The second revolution was brought about by the invention of handicrafts which gave rise to different classes of artisans, cottage industries and the development of metallic industries. The third great revolution began with the Industrial Revolution of the last century. This has given rise to the factory system, employment of men in highly organised groups and control of the whole natural resources of the country by the totalitarian state. It began with the application of the results of scientific discoveries to problems of supply of human demands and needs by private parties, but gradually as a result of competition between different countries and due to new discoveries in science, it has been found that private individuals or parties are unable to cope with all the economic, social, and scientific problems which this great process of industrialisation or technocracy has given rise to. In every country the Government has to take upon itself the need for co-ordinating the industrial activities of the different members of the society. A new system is gradually emerging in every country the full effect of which we see in Russia. Before the War, Russia was a purely agricultural country like India ; 90 per cent. of her population lived in villages and depended entirely upon agriculture. As far as industries were concerned, they were mostly in the hands of foreign capitalists. The Russian people had practically very little knowledge of technics of modern industries and arts. As a result of the revolution of 1918, a new programme of industrialisation was undertaken. The development of power and the industrial system, and of the mines have all been taken over by the Government in the so-called Five Year Plan. The result of this planned action is seen in the tremendous strides which Russia has made in Technology and Industry within the last ten years. Before the War, the total production of electricity in Russia was only 5 or 6 billion units. Within the last 5 years it has become nearly 25 billion units and it is higher than that of any other country in Europe except Germany. It has already outstripped the

production of electricity in England and I think in a few years to come, it will reach the figures of America. All this is the result of Lenin's pet idea that Russia should be electrified.

Even in England where people believe more in private enterprise, the inevitable logic of circumstances has shown that no industry can survive in the face of competition unless there is a scheme of co-operation between the scientists, the government and the industrialists. The result is the establishment of the Department of Scientific and Industrial Research. This is a scheme of organised research in which industrialists are invited to co-operate with the departments of Government and professors in the Universities, in the engineering colleges and other places. A detailed scheme of research is planned and is distributed amongst the workers on the subject who are handsomely provided with funds for research. As a result of the researches carried out in this department, the British industry has made a great recovery and effected substantial progress within the last few years and is rapidly gaining the lost ground. It is to be noticed that this department, though brought into existence by the Government has a constitution which provides for an ample representation of non-officials as well as of the representatives of industrialists. The Government controls its activities but does not hamper it. The Board is presided over by the famous physicist, Lord Rutherford, and a review of its activities may be read in *Science and Culture.*

In this country also the Government has established a department of industrial and scientific research. But the organisation of this department leaves much to be desired. It is an entirely Government concern, presided over mostly by civil servants and co-operation by University workers and private bodies is not encouraged. Now civil servants may be excellent agents for maintaining law and order, or running the wheel of justice, but it is our experience that they have not the mental equipment to plan out and organise research work on any branch of human activity. The organisation of this department is a sad contrast to that of the Agricultural Research Council in which the Government departments, the various agricultural interests in the country, the professors in non-official universities are properly represented. In the I. A. C. a scheme of co-operative research has been planned, and grants are liberally given to such professors as can submit a suitable scheme and have shown aptitude for carrying on a particular line of research. It is beyond our powers of comprehension why such a sensible scheme of co-operation has not been devised for the department of industrial and scientific research, and why it has been left entirely to the care of civil servants who are too much engrossed in routine work. If this department be properly organised, it will certainly be able to employ a large number of physicists.

NEED FOR ENDOWMENTS FOR RESEARCH IN PHYSICS.

In the beginning, I have already told my audience that the lot of the meritorious physics students who are being trained as research workers is very gloomy at the present time. On account of the unsympathetic attitude of the Government towards scientific research, there are practically no avenues of employment in which the special knowledge of the trained scientist can be utilised. I would, therefore, plead that the rich men in this country should come forward with endowments in the different universities for fellowships, so that these promising students can devote a number of years in solving particular problems. It is no exaggeration to say that the few active centres of research in India are mostly due to private endowments. The University College of Science, which started scientific work on a new basis after the war, in Calcutta was established by the princely donations of Sir T. N. Palit, Sir Rashbehari Ghose, the Raja of Khaira and the Indian Association for the Cultivation of Science which developed into an active centre of research under Professor Sir C. V. Raman was established in 1876 by a private medical practitioner of Calcutta, Mahendralal Sircar. The Indian Institute of Sciences which now contains a department of research in physics owes its existence to the princely donation of the late Mr. J. N. Tata. The Physical Laboratory in the Andhra University is due to the munificence of the Maharaja of Jeypore in the Madras Presidency. The Physical Laboratories in the Muslim and the Hindu Universities are largely the results of private benefactions. The Government has, of course, after the educational reforms of 1922-23 taken steps in re-organising Government Colleges like those at Allahabad, Dacca and Lahore on a modern basis. But this spell of progressiveness lasted, at best, for a year or two and after that the Government officials and politicians, in order to hide their incapacity for dealing with the problems of unemployment, have been sedulously preaching the doctrine that higher education and research are harmful to the nation. At the present time, there is no central fund from which a promising scholar in physics can be helped with a research grant or with a fellowship. It is well-known that without such scholarships and fellowships and research grants no advancement can be made. We are all admiring now-a-days the great advances which have been made in the physical and other sciences in the United States of America. But people in this country do not realise how much these advances are due to the great endowments like those of Rockefeller and Carnegie. As a matter of fact, but for these great endowments for research, and if left to Government alone, the United States of America would not have attained a much higher level than those of the Latin American countries. The Indian physicists have shown a great promise and it is the duty of the people to support them so that they can not only make a substantial contribution to the stock of human knowledge, but can also devote their knowledge to the solution of industrial and economic problems peculiar to India.

INDUSTRIAL RESEARCH CAN ONLY BE MADE SUPPLE-
MENTARY TO FUNDAMENTAL RESEARCH.

A class of critics has arisen in this country who hold that the professors in the universities should devote their time in carrying out investigations on only industrial problems and should not waste their time on fundamental researches

This argument is entirely fallacious. No industrial research can be carried out unless the worker has a sound grasp of the fundamentals of science. It is the duty of every university teacher first and foremost to train his students in the fundamentals of the basic sciences and to acquaint him with the latest developments in his subject. He will, therefore, be failing in his duty if he neglects pure science. Any industrial research work which can be undertaken by him can only be supplementary to his main activities. An analysis of the present conditions in the country shows that there is at present a great surplus of trained physicists who can devote their time to industrial research provided small grants can be found for them in the form of fellowships and research grants. This policy was advocated by the Unemployment Committee presided over by the Rt. Hon'ble Sir Tej Bahadur Sapru. But the recommendations of the Committee did not find favour with the Government. It is the duty of the public to come forward with offers of help to the Universities.

DUTY OF THE INDIAN PHYSICAL SOCIETY.

The Indian Physical Society is only a child of three years. It has still to develop and to prove its worth to the country. It is therefore necessary that it should take steps for an organisation of the physicists on a proper basis and try to impress upon the public the importance of physical research for the future of national reconstruction. It should try to get endowments and establish research funds for the encouragement of the younger physicists and for providing them with a berth in life. I hope that in the years to come all this will happen and the Indian Physical Society will be as useful an institution as the much older societies in Germany, England and America.

ON THE RELATION BETWEEN THE EMISSION SPECTRA OF ND+++ IONS IN PHOSPHORES AND THE ABSORPTION SPECTRA OF THE SAME IN CRYSTALS*

By P. C. MUKHERJI.

ABSTRACT. The relation between the emission spectra of Nd+++ ions incorporated into colourless ground materials like K_2SO_4, CaO, etc., and the absorption spectra of the same ion in crystals is discussed. Both kinds of spectra are shown to consist of distinct groups of more or less sharp lines. A classification of the absorption spectra of Nd+++ ions in crystals, as carried out by the writer previously, is given in which electronic transitions are assigned for the separate groups of lines, one for each group. In accordance with this, electronic transitions are proposed for interpreting the groups of emission lines. The possible transitions are discussed in the light of Van Vleck's theory of the absorption spectra of the rare earth ions in solids. The phosphorescent radiations emitted are regarded wholly quadrupole in nature and the corresponding selection rules are utilised in the assignment of transitions. The proposed transitions explain qualitatively the position of the groups, the intervals between them and their relative intensities. Some of the rare earth ions show line fluorescence in pure condition whether in solution or in crystals; the absence of such fluorescence in the case of Nd+++ ions is discussed.

The line emission spectra of the rare earth ions in solids and in solid solutions, *viz.*, the phosphores, have been widely investigated by Tomaschek and his collaborators.[1] In pure solids the visible fluorescence spectra were found to consist of fairly sharp lines at low temperatures, and like the absorption spectra of the same ions in hydrated crystals they divided into distinct groups. It was noticed by these authors that, in general, there is a relation between the emission and absorption spectra of the same ion and they are supposed to arise from a similar type of electronic transitions. Gobrecht[2] recently extended these investigations to the infra-red side and interpreted the origin of the groups of lines as due to transitions from an excited state of the 4*f*-electrons to the different levels of the ground term multiplet. But this kind of fluorescence has not been found to occur in all the ions of the rare earth group; only in four out of the fourteen, *viz.*, in Sm, Eu, Tb and Dy, which are symmetrically placed with respect to Gd, this was observed.

The other kind of emission spectra, *viz.*, that given out by the rare earth ions present in phosphores, are known in cases of almost all the ions of the group with

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the exception of Ce.$^{+++}$ The phosphores are prepared by incorporating a minute quantity of the pure salt in colourless ground materials (generally consisting of the oxides and sulphides of the alkaline earth metals) and when excited by strong ultra-violet light or by a beam of cathode rays they give out characteristic spectra. These phosphorescent spectra are very rich in lines, which are extremely sharp even at the ordinary temperature. For those ions which emit both the fluorescent and phosphorescent spectra the centres of the groups of lines emitted were found to coincide nearly, although each group in the latter was somewhat more spread out. This has been regarded as indicating that same electronic transitions were responsible for the two types of emission spectra, while the difference in their finer structure was to be attributed to the influence of the environments in which the ions were placed in the respective cases. Gobrecht has recently analysed the phosphorescent line spectra of Pr^{+++} on this hypothesis. In this paper it is proposed to interpret the spectra emitted by Nd-phosphores on similar lines.

THE ABSORPTION SPECTRA OF Nd^{+++} IONS IN CRYSTALS.

The absorption spectra of Nd^{+++} ions in crystals were partially classified by the writer in a previous communication.[3] Each group of absorption lines was supposed to be due to a single electronic transition from the ground level to an upper excited level in the $4f$-shell; the finer structure inside the groups was assumed to be due to the Stark-splitting of the energy levels as well as to the superposition of lattice oscillations. In Nd^{+++} ions containing three $4f$-electrons the terms allowed by Russell-Saunders coupling are given by $^4(S, D, F, G, I)$ and $^2(P, D, F, G, H, I, K, L)$. The relative positions of the levels of same multiplicity may be denoted according to Hund's rules by

$$^4S > {}^4D > {}^4F > {}^4G > {}^4I \text{ for the quartets}$$

and similarly for the higher doublet levels. Again, the multiplets being all normal here, the ground level, which is the lowest level of the ^4I state, is to be denoted by $^4I_{\frac{9}{2}}$. In the process of absorption, an electron was assumed to jump from this basic level to the components of upper quartet and doublet states, according to the rules of selection laid down for quadrupole and other higher order radiations. In table I the frequencies of the C.G.s' of the groups of absorption lines and the corresponding transitions are given. If the ground term $^4I_{\frac{9}{2}}$ represent the zero in the energy scale, the frequencies given in table I correspond to the absolute energy values of the upper levels, and it is possible to construct with them the energy level diagram for the ions in question.

TABLE I.

C. G. of the groups.	Int.	Transitions assigned.	Changes in L and J.
I			
(i) 11,553 cm^{-1}	weak	$^4I_{9/2} \rightarrow ^4G_{5/2}$	$-2; -2$
(ii) 12,509 ,,	strong	$\rightarrow ^4G_{7/2}$	$-2; -1$
(iii) 13,534 ,,	,,	$\rightarrow ^4G_{9/2}$	,, ; 0
(iv) 14,791 ,,	fair	$\rightarrow ^4G_{11/2}$	,, ; +1
II			
(i) 15,980 ,,	weak	$^4I_{/2} \rightarrow ^4F_{5/2}$	$-3; -2$
(ii) 17,120 ,,	strong	$\rightarrow ^4F_{7/2}$	,, ; -1
(iii) 18,900 ,,	,,	$\rightarrow ^4F_{9/2}$	,, ; 0
(iv) 19,622 ,,	fair	$^4I_{9/2} \rightarrow ^4D_{5/2}$	$-4; -2$
(v) 21,103 ,,	strong	$\rightarrow ^4D_{7/2}$	$-4; -1$
III			
(i) 24,757 ,,	weak	$^4I_{9/2} \rightarrow ^2H_{9/2}$	$-1; 0$
(ii) 28,486 ,,	fair	$\rightarrow ^2G_{7/2}$	$-2; -1$
(iii) 30,412 ,,	,,	$\rightarrow ^2H_{11/2}$	$-1; +1$
(iv) 33,049 ,,	weak	$\rightarrow ^2G_{9/2}$	$-2; 0$
III			
v) 34,201 Cm^{-1}	weak	$^4I_{9/2} \rightarrow ^2F_{5/2}$	$-3; -2$
vi) 38,283 ,,	,,	$\rightarrow ^2F_{7/2}$	,, ; -1
vii) 39,759 ,,	very weak	$\rightarrow ^2D_{3/2}$	$-4; -3$
viii) 42,375	very weak	$\rightarrow ^2D_{5/2}$	,, ; -2

In a few transitions in table I there are departures from the selection rules of quadrupole radiation. These are possible according to Van Vleck only in strong asymmetric crystalline fields and will be discussed later.

THE EMISSION SPECTRA OF Nd^{+++} IONS IN PHOSPHORES.

The emission lines of Nd-phosphore recorded by Tomaschek under different modes of excitation are given in tables II(a) and II(b). In table II(a) the lines from K_2SO_4Nd under optical excitation are entered and they form only one group of lines in the near infra-red. Table II(b) contains the lines obtained from

CaO-Nd phosphore excited by means of cathode rays. It is found that the lines are much more numerous when the phosphore is bombarded by a beam of cathode rays, *e.g.*, the lines in table II(*b*) give rise to several groups in addition to the group in the near infra-red contained in II(*a*). On comparing the wavenumbers of the infra-red lines present in both the tables it will be noticed that they do not, in general, agree. This is of course expected when the ground materials in the two cases are different. In addition to the lines emitted by the phosphores, the emission lines of Nd-glass are also given in the table II(*a*).

TABLE II(*a*).

Infra-red lines from K_2SO_4Nd (at $-180°$).

'ν'		Int		C.G. of the group.	
11,120	cm^{-1}	4			
201	,,	3			
286	,,	2			
387	,,	3		11,320 cm^{-1}	
429	,,	3			
444	,,	2			
482	,,	6			
513	,,	4			
564	,,	2			
*11,396—					
11,266	,,	strong band		11,332 ,,	

* Emission from Nd-glass (at $-180°$)

TABLE II (b).

Emission from CaO. Nd. (at + 20°).

	Int.	C.G.		Int.	C.G.
10,609 Cm^{-1}	3		21,316 Cm^{-1}	w	
657 ,,	3		453 ,,	m	
711 ,,	4		686 ,,	w	21,730 cm^{1}
760 ,,	4		852 ,,	st	
880 ,,	2		22,142 ,,	w	
965 ,,	2	11,000 cm^{-1}	721 ,,	w	
11,082 ,,	6				
196 ,,	10		23,276 ,,	v.st	
296 ,,	10		413 ,,	—	
382 ,,	3		634 ,,	v.st.	
			690 ,,	st.	23,586 ,,
11,695 ,,	2		860 ,,	st	
736 ,,	3				
786 ,,	2		25,118 ,,	st.	25,310 ,,
874 ,,	2		503 ,,	st.	
909 ,,	1				
12044 ,,	4		36,446 ,,	m	
163 ,,	5	12,140 ,,	619 ,,	m	
211 ,,	1		985 ,,	m	
288 ,,	3		37,136 ,,	st	
334 ,,	2		261 ,,	m	
477 ,,	2		568 ,,	m	37,028 ,,
584 ,,	2		611 ,,	m	
13,206 ,,	2	13,276 ,,			
346 ,,	2				

In table III a classification of these emission lines is proposed as arising out of transitions between term levels of the Nd^{+++} ions which were obtained from an analysis of its absorption spectra. The table contains the C. G.'s of

the different line groups, their average intensities, the proposed electronic transitions and the corresponding frequencies as calculated from the absorption data.

TABLE III.

C. G. of the groups.	Int.	Transitions possible.	Changes in 'L' and 'J'.	Calculated from absorption.
I.				
(a)　11,332 Cm^{-1}				
(b)　11,320　,,	v strong	$^4G_{\frac{5}{2}} \longrightarrow {}^4I_{\frac{9}{2}}$	$+2$; $+2$	11,552 Cm^{-1}
11,000　,				
II.				
12,140　,,	weak	$^2H_{\frac{9}{2}} \longrightarrow {}^4G_{\frac{7}{2}}$	-1 ; -1	12,236　,,
13,276　,,	v. weak	$\longrightarrow {}^4G_{\frac{5}{2}}$	-1 ; -2	13,192　,,
III.				
21,730　,,	medium	$^2H_{\frac{9}{2}} \longrightarrow {}^4I_{1\frac{3}{2}}$	$+1$; $+2$	—
23,586　,,	strong	$\longrightarrow {}^4I_{1\frac{1}{2}}$	$+1$; $+1$	—
25 310　,,	medium	$\longrightarrow {}^4I_{\frac{9}{2}}$	$+1$; 0	24,745　,,
IV.				
(c)　27,129　,,	weak	$^2G_{\frac{7}{2}} \longrightarrow {}^4I_{\frac{9}{2}}$	$+2$; 1	28,475　,,

(a) Emission spectra of Nd-glass excited by light.
(b)　　　Do　　　of K_2SO_4 – Nd　,,　　do.
(c) Additional group emitted by Al_2O_3 – Nd under cathode ray excitation

DISCUSSION.

It is found that the majority of the groups of emission lines conform to the scheme of classification shown above, which is very similar to that adopted for the absorption spectra ; also they are capable of being represented by transitions in the energy level diagram constructed for Nd''' ions from the absorption data as shown in figure 1. In both of these cases, *viz.*, emission and absorption, the changes which ' L ' and ' J ' undergo in each transition are given in the

corresponding table. It is found that according to the selection rules given by Laporte most of the specified transitions are forbidden. They can thus hardly be expected to give rise to lines of appreciable intensity, observed in absorption as well as in emission.

Recently Van Vleck[1] has discussed this question with special reference to the absorption spectra of the rare earth ions in solids. He regarded the transitions as all more or less forbidden in ordinary dipole radiation and calculated the probability of transition in all the other forms of radiation, which the ions can possibly emit under the influence of the crystalline field. These are tabulated below together with the allowed changes of 'L' and 'J' in each case.

TABLE IV.

Forms of radiation	Selection rules.	
1. Quadrupole	$\Delta L = 0, \pm 1, \pm 2$ $(0 + \longrightarrow 0)$	4 sec$^-$
	$\Delta J = 0, \pm 1, \pm 2$ $(0 + \longrightarrow 0, 1)$	
2. Magnetic Dipole	$\Delta L = 0, \pm 1$ $(0 + \longrightarrow 0)$	
	$\Delta J = 0, \pm 1$ $(0 + \longrightarrow 0)$	
3. Electric Dipole (caused by distortion of the electronic motion due to crystalline fields).	Δl or ΔJ may be equal to even 4 or 5	(a) 1 sc (no centre of symmetry)
		(b) 1'0 ,, (dissymmetry caused by vibration).

As shown in the table the probability of transition is very low in each case being of the order of about one-millionth of that in the ordinary dipole radiation. This is in agreement with the experimental results of Becquerel,[5] who found that the intensity of absorption of these ions (specially Pr^{+++} and Nd^{+++}) is extremely low and obtained values of $\sigma \cap$ 10 to 100 sec^{-1}. They are of the same order of magnitude as in the four cases cited above, as according to Van Vleck the calculation may be easily out by the order of 10 to 100. The apparent intensity of the absorption lines is due to the high concentration of the ions in the solid crystals.

In the case of emission spectra it is sufficient to assume that their origins are due to quadrupole radiation involving changes of 'L' and 'J' not greater than 2 units. In the case of the absorption spectra on the other hand, the origin of certain faint lines have been found to involve larger changes of these two quantum numbers and are according to the views of Van Vleck to be ascribed to electric dipole radiations arising out of forbidden transitions in an unsymmetrical crystalline electric field. Van Vleck has discussed two different ways in which such a field can arise. In emission the electronic transition usually occurs

between the excited states and the different levels of the ground term. But it will be noticed that the transitions do not take place from all the different levels of the upper multiplets but only from their lowest levels. The electron, when in any one of the upper level, is first brought down to the lowest level of the multiplet in question by thermal collisions, and from there it jumps back to the ground state. Many of the transitions possible in absorption do not therefore appear in emission ; thus it is possible to find out the multiplet separations of many of the upper states from the absorption data, but the emission data help only in obtaining the same for the ground state. In table III the possible transitions obeying the rules of quadrupole radiation are given. In the following it will be seen how far they can explain the intensity of the different groups as also the intervals between them. For convenience we shall divide the transitions assigned into three classes, *viz.*,

(*a*) Transitions among the quartet levels : In the table only one such transition is specified, *viz.*, ${}^{4}G_{\frac{5}{2}} \longrightarrow {}^{4}I_{\frac{9}{2}}$. It is easy to see that other transitions of this type are all excluded, since transitions from ${}^{4}G_{\frac{5}{2}}$ to other levels of ${}^{4}I$ will involve a change in '*J*' by more than two units while in transitions from other quartet levels both '*L*' and '*J*' will have to change by more than two units. The intensity of this group is the highest as shown in the table. This is to be anticipated, because in this transition there is not only no change of multiplicity but also the changes in *L* and *J* are in the same sense.

(*b*) Transitions from the doublet levels to the ground state. The allowed transitions of this kind are

(*i*) ${}^{2}H_{9} \longrightarrow {}^{4}I_{\frac{9}{2}, \frac{11}{2}, \frac{13}{2}}$.

(*ii*) ${}^{2}G_{\frac{7}{2}} \longrightarrow {}^{4}I_{\frac{9}{2}, \frac{11}{2}}$.

In the table the three groups corresponding to (*i*) are given. It is expected that the intervals between these groups should give the splitting of the ground term multiplet. The separations between these levels calculated according to the well-known formula are given by

$$\Delta \nu \, ({}^{4}I_{\frac{9}{2}} \longrightarrow \tfrac{11}{2}) = \quad 1814 \text{ cm}^{-1}$$

$$\Delta \nu \, ({}^{4}I_{\frac{11}{2}} \longrightarrow \tfrac{13}{2}) = 2144 \,,, \qquad ,$$

f it be assumed that the screening constant $\sigma = 34$. The corresponding intervals from the table III will be found to be 1724 cm^{-1} and 1856 cm^{-1} respectively, showing thereby a fair agreement. The relative intensities of the groups are also in accordance with the theory for the middle group where both '*L*' and '*J*' increases by '1' is stronger than the other two where '*J*' either remains same or increases by 2 units. Of the remaining transitions in (*ii*) only one is

FIGURE 1.

Energy level diagram for Nd^{+++} ions which accounts for several of the observed frequencies of absorption and emission spectra of the ion.

(a) For absorption in crystals.

(b) For emission from phosphores.

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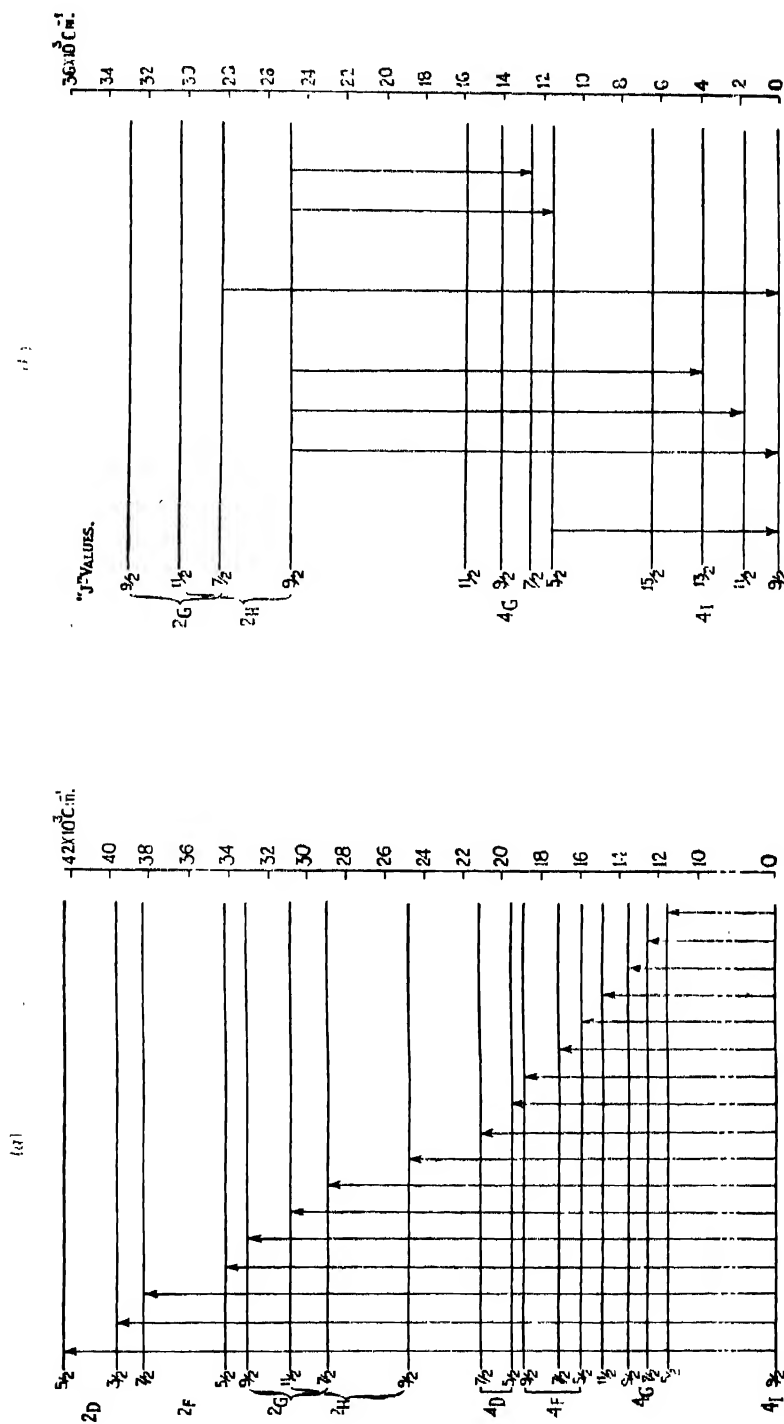
present in the table, which gives rise to a group of weak lines observed only in $Al_2O_3 \cdot Nd$.

(c) Transitions where the final level is an excited level: The table contains two such transitions, viz., $^2H_{\frac{9}{2}} \longrightarrow {}^4G_{\frac{5}{2}, \frac{7}{2}}$. The frequency interval between the corresponding groups of lines agrees fairly well with the separation between the $^4G_{\frac{5}{2}}$ and $^4G_{\frac{7}{2}}$ levels, as obtained from the absorption data. The probability of such transitions is, however, very low from what has been said above, and this is shown by the extremely low intensity of these groups of lines, although the changes in ' L ' and ' J ' are quite favourable.

In the above portion we have seen that there is a good deal of similarity between the absorption and the emission spectra of Nd^{+++} ions, even when in different states of aggregation. But there are also a few points of distinction between the two and it seems desirable to discuss them here. It is found that although the general nature of the absorption spectra remains practically same whether the Nd^{+++} ions are in solutions or in crystals, or whether they are embedded in glass or other colourless ground meterials, it makes a lot of difference in emission. Thus whereas the Nd^{+++} ions in glass or in the phophores give rise to the groups of emission lines in the visible, the pure ions whether in solution or in crystals have not been found to emit any. This naturally leads one to postulate the influence of the foreign atoms present in bringing about the corresponding transitions in emission. But such an assumption will not in general be valid for all the rare earth ions, as it has already been referred to above that some of these show line fluorescence in pure condition whether in solution or in crystals. On the other hand, many of the transitions shown in the energy level diagram in figure 1 are reversible appearing both in the process of absorption and emisssion, which indicates that the corresponding radiations should behave more or less like the resonance radiation of free atoms. It seems thus extremely difficult to explain why there will be no line fluorescence in ions like Nd^{+++} when in pure condition either in solution or in crystals.

In conclusion, the writer desires to express his grateful thanks to Prof. D. M. Bose for his kind interest and helpful discussions in course of the work.

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VERIFICATION OF STOKES' THEORY OF A SPHERE OSCILLATING IN A LIQUID.

(By means of an oscillating float)

By D. S. SUBRAHMANYAM, M.A.*

ABSTRACT. A float is constructed of a hollow sphere and a fine uniform stem and made to oscillate in water up and down, the sphere being under water and the stem passing through the surface. From the period and logarithmic decrement of the float, the virtual mass of the sphere is calculated which is found to be in good agreement with the value obtained by Stokes theory. Secondly, assuming Stokes theory to be true, the coefficient of viscosity of water is calculated which again is found to agree with the capillary flow value, when correction is made for the damping due to the stem. Thus Stokes' theory of a sphere oscillating in a liquid is fully verified.

1. INTRODUCTION

It is a well-known fact that when a floating body is displaced upwards or downwards from its equilibrium position and released, it performs oscillations which are rather quickly damped. When suitably devised, these oscillations can be made to be very helpful in studying some very interesting problems connected with the motion of solids in fluids. When a solid body moves in a fluid it appears to possess a mass (called virtual mass) greater than its own and it also experiences a resistance due to the relative motion set up between different parts of the surrounding fluid Stokes [1] gave a theory of a solid sphere performing small linear oscillations in a viscous fluid and tried to substantiate it from the experimental results of Bassel and Baily [2] on pendulums. He found his theory to be very satisfactory in the case of pendulum balls swinging in air, but in the case of pendulums swinging in water the results were not conclusive. Stokes' theory had attracted the attention of some scientists recently who tried to test its validity. Mc.Ewen [3] measured the force acting on a sphere in water and in a very viscous oil by a forced vibration method, the forcing being done by a mechanical arrangement. He obtained for the coefficient of viscosity of water, η, the value 0.0091 at 16.5° C. which is too low as compared to the value 0.0111, obtained by the capillary flow method. Barnes [4] estimated the

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increase in the inertia of a sphere by making a ballistic pendulum receive a peudulum ball moving under water. The increase in the inertia of a body is usually expressed as K times the mass of the fluid displaced by it. Krishnayar [5] determined the value of K of oscillating spheres by attaching the sphere to a fine wire which is made to vibrate by an electrical method He employed balls of diameters 1·7 cm., 1.36 cm., and 1·7 cm and obtained for K the values 0·584, 0.585 and 0.580 respectively. The corresponding values calculated according to Stokes' theory are 0.53, 0.536 and 0.530 respectively.

Stokes' theory had also been put to experimental test by F.E.Hoare [6] who found that the logarithmic decrement of a pendulum ball oscillating in water gradually diminishes with time, thereby showing that one of the assumptions made by Stokes (that frictional resistance is proportional to velocity) is not valid. Brindley and Emerson, [7] however, find that the above assumption is valid when the amplitude is sufficiently small, (less than 0.5 cm.). Calculating on the basis of Stokes' theory they find that $\eta = 0.0131$ at $15.5°$ C , whereas the generally accepted value at that temperature is 0.0113. They conclude that the higher value is due to the suspending wire and working with two and three wires arrive at a correction which is to be applied to the logarithmic decrement observed with one wire. Making this correction they get values (0.0116, 0.0114, etc.) which are in fair agreement with the capillary flow value mentioned above.

It is thus seen that the experiments made so far aim at determining either the virtual mass or the damping but not both at the same time Moreover, there has been no satisfactory verification of Stokes' theory in regard to virtual mass. The oscillating float can be made to give results both in regard to virtual mass and damping, and may therefore be employed to test Stokes' theory fully.

2. THEORY OF THE OSCILLATING FLOAT.

Let a floating body be made up of a hollow vessel B to which is attached a fine stem A of uniform cross-section and let it be suitably loaded so as to float upright with the hollow vessel B and a part of the stem A under water. If the float be now given a small vertical displacement and released, it begins to oscillate up and down, the amplitude of oscillation gradually decreasing.

The period of oscillation of the float may be easily calculated. Let a be the area of cross-section of the stem, ρ the density of the liquid, g the acceleration due to gravity, V the volume of the vessel, B, and h the height of the stem from its lower end to the surface of the liquid in the equilibrium position of the float. When the float is displaced vertically upwards through a small height x from its equilibrium position (without causing any rotation), the upward force acting on the float is equal to the height of the displaced liquid, i.e., to $\{V + a(h - x)\} \rho.g.$ The downward force on the float is equal to its weight which in turn is equal to

$(V + ah) \rho . g .$, the weight of the displaced liquid when it is in equilibrium. Hence, there is a resultant force acting on the float, which is equal to $a \rho g x$ and which is opposite in direction to its displacement.

Let us assume that the surface of the liquid exerts no restoring force on the float as the stem moves up and down through it. As the oscillations are damped let us assume further that a resistance is offered to the motion of the float due to the viscosity of the liquid which is proportional to the velocity of the float. Let this be represented by $K'M' \dfrac{dx}{dt}$, where M' is the mass of the displaced liquid, and K' is a constant. The virtual mass of the float then becomes $(M + K_1 M')$ where M is the mass of the float and $K_1 M'$ the apparent increase in the inertia of the float due to the circulation set up in the liquid as the float moves in it. The equation of motion may then be written down as :

$$(M + K_1 M') \frac{d^2 x}{dt^2} = - a \rho g x - K'M' \frac{dx}{dt}$$

If m be written for the virtual mass $(M + K_1 M')$ the above equation may otherwise be stated as :

$$m \frac{d^2 x}{dt^2} = - a \rho g x - K'M' \frac{dx}{dt}$$

$$\text{or} \quad m \frac{d^2 x}{dt^2} + K'M' \frac{dx}{dt} + a \rho g x = 0 \qquad \qquad \ldots \text{ (1)}$$

As is well known, when $(K'M')^2 - 4 \, m a \rho g$ is a negative quantity, the solution of this equation is

$$x = A e^{-pt} \cos (\omega t + a)$$

where $\qquad p = \dfrac{K'M'}{2m},$

$$\omega = \left(\frac{a \rho g}{m} - p^2 \right)^{\frac{1}{2}} = \left\{ \frac{a \rho g}{m} - \left(\frac{K'M'}{2m} \right)^2 \right\}^{\frac{1}{2}}$$

and A and a are arbitrary constants.

The float will therefore experience damped S.H.M. the period of oscillation, T, being given by the relation

$$T = \frac{2\pi}{\omega} = 2\pi \left\{ \frac{a \rho g}{m} - \left(\frac{K'M'}{2 \, m} \right)^2 \right\}^{\frac{1}{2}} \qquad \qquad \ldots \ldots \text{ (2)}$$

The logarithmic decrement λ is equal to $p \dfrac{T}{2}$ or substituting the value of p.

$$\lambda = \frac{K'M'}{2m} \cdot \frac{T}{2} = \frac{K'M'T}{4m} \qquad \cdots \text{ (3)}$$

Equations (2) and (3) enable us to determine the virtual mass m and the frictional resistance factor k. Equation (2) may be written down also as

$$\frac{4\pi^2}{T^2} = \frac{a\rho g}{m} - \left(\frac{K'M'}{2m} \right)^2$$

But from (3) we have

$$\left(\frac{K'M'}{2m} \right)^2 = \frac{4\lambda^2}{T^2}$$

$$\therefore \qquad \frac{4\pi^2}{T^2} = \frac{a\rho g}{m} - \frac{4\lambda^2}{T^2}$$

or

$$\frac{a\rho g}{m} = \frac{4\pi^2}{T^2} \left(1 + \frac{\lambda^2}{\pi^2} \right)$$

From this we get the result

$$m = \frac{a\rho g T^2}{4\pi^2 \left(1 + \dfrac{\lambda^2}{\pi^2} \right)} \qquad \cdots \text{ (4)}$$

If r be the radius of cross-section of the stem, $a = \pi r^2$ and then equation (4) becomes

$$m = \frac{r^2 \rho g T^2}{4\pi \left(1 + \dfrac{\lambda^2}{\pi^2} \right)} \qquad \cdots \text{ (5)}$$

When the virtual mass, m, is obtained from this equation, the factor K_1 can be calculated from it because we have

$$m = (M + K_1 M')$$

It should be noted however that M is the mass of the float, M' the mass of the displaced liquid (including that displaced by the stem) and K_1 the factor for the sphere and the stem together. Strictly speaking this will differ from the factor, K, for a sphere. But, since the mass of water displaced by the stem is very small and since the stem moves in the direction of its axis, the increase in the inertia of the system due to the stem may be neglected and the increase considered to be due to the sphere only. If K expresses the factor for the sphere and M the mass of the liquid displaced by the sphere alone, according to what has been stated, the increase in inertia will be equal to KM''

and

$$m = M + KM'' \qquad \qquad \dots (6)$$

If m_2 is the mass of the liquid displaced by the portion of the stem under the liquid when the float is in the equilibrium position, the total mass of liquid displaced in this position M' is equal to $M'' + m_2$. But from the law of floating bodies, M'=M. Hence $M = M'' + m_2$ and substituting this value in (6) above we get

$$m = M'' + m_2 + KM''$$

or

$$M'' (1+K) = m - m_2$$

or

$$K = \frac{m - m_2}{M''} - 1 \qquad \qquad \dots (7)$$

This equation enables us to determine K.

The internal friction factor K' can be calculated from equation (3)

$$K' = \frac{4m\lambda}{M'T} \qquad \qquad \dots (8)$$

If λ and T are observed for the float, and m is obtained from (5) we can determine the value of K' from (8).

We may test Stokes' theory by giving to the hollow vessels, B, the shape of a sphere. According to Stokes the force, X, acting on a sphere oscillating in an infinite mass of liquid is

$$X = -M'' \left(\frac{1}{2} + \frac{9}{4\beta R} \right) \frac{d^2 x}{dt^2} - \frac{9}{4} M'' \sigma \left(\frac{1}{\beta R} + \frac{1}{\beta^2 R^2} \right) \frac{dx}{dt}, \qquad \dots (9)$$

where M'' is mass of the liquid displaced by the sphere,

$\beta = \sqrt{\dfrac{\pi\rho}{\eta T}}$, η being the viscosity of the liquid, ρ the density, and T the period of oscillation, $\sigma = \dfrac{2\pi}{T}$ and R is the radius of the sphere.

The first term on the right-hand side of equation (9) gives the correction for the inertia of the sphere and the second term the internal friction factor. Hence according to Stokes,

$$K = \frac{1}{2} + \frac{9}{4\beta R} \qquad \qquad \dots (10)$$

and
$$K = \frac{9}{4}\sigma\left(\frac{1}{\beta R} + \frac{1}{\beta^2 R^2}\right) \qquad \dots (11)$$

If the value of K obtained from (7) agrees with that calculated from (10) and the value of K' obtained from (8) agrees with that from (11), Stokes' theory is to be taken to be true   This is the procedure adopted in regard to K, but a slight modification is made with respect to K'   In this case, the value of the coefficient of viscosity, η, is calculated assuming Stokes' theory to be true, *i. e.*, equating the right-hand sides of equations (8) and (11). If the value of η so obtained agrees with the value obtained by other methods, Stokes' theory can be taken to be valid.

EXPERIMENT.

The float (represented in figure 1) prepared for the experiment consists of a hollow brass sphere, B, of radius about 5 cm. It has a small circular opening (about 0 6 cm. in diameter) through which the required quantity of lead shot could be introduced so as to make it float properly. A length of about 25 cm. of thick uniform brass-wire is taken and its lower end passed through the circular opening of the sphere and soldered such that its axis is directed towards the centre of the sphere. Care is taken to see that the portion closed with solder is even with the rest of the surface of the sphere. In the experiment four such stems of different diameters are used, firstly to obtain different periods of oscillation and secondly to investigate the effect of the stem on the
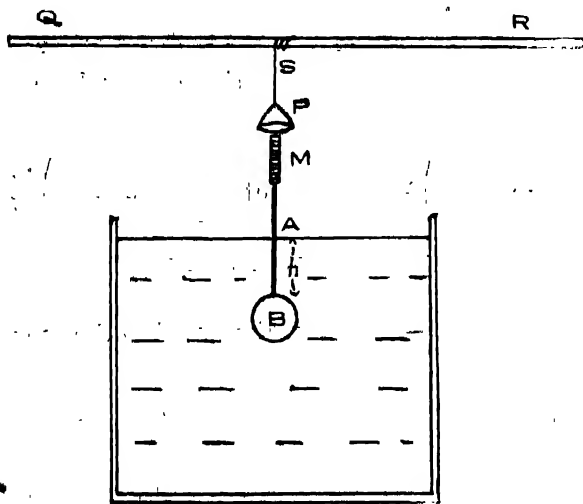
FIGURE 1.

motion of the float. At the top of the stem is attached a small pan P in which small weights can be placed so as to make the float sink to any desired point on the stem. A light millimeter scale, M of length about 8 cm. is attached to the upper part of the stem, with the help of which the turning points of the float as it oscillates up and down are observed. A reading telescope is employed for this purpose and it is kept at a distance of about $1\frac{1}{2}$ meters from the scale. The float is kept in a tank of water about $5' \times 3' \times 1\frac{1}{2}'$ in a closed room from which draughts of air are excluded. It is assumed that the tank is big enough for the circulation of water to stop before reaching its walls. The float is initially slightly displaced upwards and tied to a fixed horizontal bar QR by means of an unspun silk fibre, S. After the float has become perfectly stationary the fibre is burnt when the float oscillates up and down at one and the same place without rotation. It is found that the oscillations are rather quickly damped (about 10 oscillations being clearly observed); yet it has been quite possible to determine the logarithmic decrement and the period of oscillation satisfactorily in all cases.

Resistance due to internal friction proportional to velocity :—The assumption that the resistance due to the internal friction of the liquid is proportional to the velocity, leads to equation (3)

$$\lambda = \frac{K'MT}{4m}$$

Since all the quantities on the right-hand side are constant for the float with a particular stem, λ should be independent of time as the float oscillates. It is found that this is the case with each one of the stems used and below are given the observations taken in an experiment, selected at random. The amplitude in all cases is less than 2 cm. (and therefore the extent of swing from the turning point to the other less than 4 cm.). In the first column are given the extents of successive swings and in the third column the extents of swings that are obtained after an interval of 6 vibrations from those in the first column.

TABLE I.

A_1	$Log_{10}A_1$	A_7	$Log_{10}A_7$	$Log_{10}A -$ $Log_{10}A_7$	λ to base 10
2·96 cm.	0·4713	1·30 cm.	0·1139	0·3574	0·0596
2·60 ,,	0·4150	1·14 ,,	0·0569	0·3581	0·0597
2·26 ,,	0·3541	0·98 ,,	$\overline{1}$·9912	0·3628	0·0505
1·96 ,,	0·2923	0·86 ,,	$\overline{1}$·9345	0·3578	0·0596
1·70 ,,	0·2304	0·75 ,,	$\overline{1}$·8751	0·3553	0·0592
1·50 ,,	0·1761	0·66 ,,	$\overline{1}$·8195	0·3566	0·0594
				Mean	0·0597

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In this respect this experiment gives results which are somewhat different from those obtained with pendulum balls. With such amplitudes as are used in this experiment it was there found that λ decreases with time. But it should be noted that in the case of the oscillating float the period obtained is very much greater than the period in the pendulum experiments referred to above and consequently the average velocity of the body much less. The periods in the experiment range from about 14 sec. to 38·0 sec while the period in the pendulum experiments was only 5 sec. It is very difficult to obtain such long periods with a pendulum, as, for example, it will require a wire of length about 150 metres to obtain a period of 25 sec. In this respect the oscillating float experiment has a distinct advantage over the pendulum experiment for investigating the validity of Stokes' theory.

VIRTUAL MASS.

Determination of K:—Below are given in a tabular form the results of the experiments made with the different stems. Mean values of T and λ are given below. The individual values of T with any stem differed from one another by less than 1% while there was as much variation as even 3% in some cases in the individual value of λ. In the last column below are given the values of K obtained by applying Stokes' theory the value of M being assumed to be 0·008216* at 28·8°C. which is the temperature of water at the time of experiment.

Equation (5) is made use of to determine the virtual mass of the float and equation (7) to determine the value of K. The density of water ρ' is assumed to be equal to 1, and g, the acceleration due to gravity at Guntur, to be 979·0 cm. sec^{-2}. The mean radius of the hollow sphere, B, is 5·107 cm. M″ the mass of the water displaced by the sphere is 558·0 gm., λ is given to the base c.

TABLE II.

Stem.	r.	T.	λ.	m	m_2	K (expt).	K (Stokes').
A	0 236 cm	14·33 sec.	0·1073	890 0 gm.	1·4 gm	0·592	0·585
B	0·1635 ,,	20·78 ,,	0·1259	898·2 ,,	0·7 ,,	0·608	0·603
C	0·1328 ,,	25 70 ,,	0·1377	904·4 ,,	0·4 ,,	0 620	0·614
D	0·0885 ,,	38·80 ,,	0·1644	916·0 ,,	0·2 ,,	0·642	0·640

The values of K is obtained from the experiment are in good agreement with the corresponding values calclutated from Stokess' theory. According to the theory K is not a constant for the same sphere but varies slightly with the period of oscillation. The results of the experiment show this variation also very satisfactorily. The experiment thus shows that the expression for virtual mass given by Stokes' theory is true. From the satisfactory way in which the theory has been verified, we may conclude that the method of the oscillating float is a very good one for determining the virtual mass of solids as they oscillate in a liquid.

VISCOSITY OF WATER.

For calculating the viscosity of water we start with equation (8):

$$K' = \frac{4m\lambda}{M'T} = \frac{4(M + KM'')\lambda}{M'T}.$$

Now, since $M = M' = M'' + m_2$ and since m_2 is less than 0.3% of M'' (see Table II) the error committed will not exceed 3 in 1000, if in the above equation we assume that $M = M' = M''$, as K itself is a factor less than 1. The accuracy of this part of the experiment cannot be claimed to be so high as this, as the mean values of λ in different experiment with the same stem differ from one another by as much as even 3 per cent. in some cases. Hence we may safely make this assumption and write down

$$K' = \frac{4(M + KM')\lambda}{M'T}$$

$$= \frac{4M'(1 + K)\lambda}{M''T}$$

$$= \frac{4(1 + K)\lambda}{T}.$$

K' is the factor which gives us the resistance offered to the float due to the internal friction of the liquid. As a first step in our calculation, let us assume that there is no additional resistance offered due to the stem but that it is all due to the sphere alone. Then we can easily equate the above value of K to that given by Stokes. Accordingly, we will have

$$K' = \frac{4(1 + k)\lambda}{T} = \frac{9}{4} \cdot \frac{2\pi}{T}\left(\frac{1}{\beta R} + \frac{1}{\beta^2 R^2}\right) \qquad \ldots \quad (12)$$

Substituting the value of K, which according to Stokes is equal to

$$\left(\frac{1}{2} + \frac{9}{4\beta R}\right),$$ and rearranging the terms, the above equation

can be reduced to the form

$$\frac{4\lambda}{3\pi} \beta^2 R^2 - \left(1 - \frac{2\lambda}{\pi}\right)\beta R - 1 = 0 \qquad \ldots (12a)$$

knowing the value of λ, βR may be first determined from this equation, and

then η. If, however, in (12a) we ignore $\frac{1}{\beta^2 R^2}$ as compared to $\frac{1}{\beta R}$ and

$\frac{9}{4\beta R}$ as compared to $\frac{1}{2}$ in substituting for K, as quantities of the second order

of magnitude, a much simpler equation is obtained.

$$\eta = \frac{16 R^2 \lambda^2 \rho}{9\pi T} \qquad \ldots (12b)$$

The values of η obtained with the different stems by making use of the
more accurate equation (12a) are given below :—

TABLE III.

Stem.	Radius of the stem.	λ (mean value).	η
A	0·236 cm.	0·1073	0·01241
B	0·1635 ,,	0·1259	0·01186
C	0·1328 ,,	0·1377	0·01153
D	0·0885 ,,	0·1644	0·01099

The values obtained for η are clearly much higher than the capillary flow
value 0·008216 at 28·8°C. In this respect, however, the experiment is not
at variance with other experiments [9] on damping which give higher values for
η than the capillary flow value. Brindley and Emerson[7] as has been already
stated, obtained 0·0131 for η from pendulum experiment whereas the value
by the capillary flow method is 0·0113. They could get a satisfactory
value when a correction is applied for the suspending wire. In a similar
way the damping due to the stem may be responsible for the high values of η
obtained in this experiment, and this is supported by the fact that the value of
η increases with the radius of cross-section of the stem (Table III).

A correction for the stem is therefore attempted in the following manner.
The damping exerted on the float may be taken to consist of two parts, firstly the
force exerted on the sphere, secondly the force exerted on the stem. The force
exerted on the sphere is evidently due to the internal friction of the liquid and
is given by Stokes' theory. The force exerted on the stem may be due to two

causes : (*i*) The damping exerted on the stem due to the internal friction of the liquid as it moves up and down in the liquid. But considering the fact that the displacement due to the stem is very small compared to the displacement of the sphere, and that the stem moves parallel to the direction of its axis, this force must be negligibly small. (*ii*) It is also quite probable that the surface of the liquid exerts a damping force on the stem as it moves up and down through it. As the surface forces act along the circumference of the stem, they must be proportional to the circumference, *i.e.*, to the radius of the stem. Hence allowance may be made for the damping due to the stem if we write a new term $p.r$ on the right-hand side of equation (12), where pr is a constant. This equation then becomes

$$K' = \frac{4(1+K)\lambda}{T} = \frac{9}{4} \frac{2\pi}{T}\left(\frac{1}{\beta R} + \frac{1}{\beta^2 R^2}\right) + pr \qquad (13)$$

or

$$(1+K)\lambda = \frac{9}{8}\pi\left(\frac{1}{\beta R} + \frac{1}{\beta^2 R^2}\right) + p.\frac{r.T}{4} \qquad \ldots \ (14)$$

Consistent with the accuracy of this part of the experiment, $r.T$. can be taken to be a constant, as in equation (5) the error in ignoring $\frac{\lambda^2}{\pi^2}$ as compared to 1 is not even 1 per cent. Hence the above equation may be written as

$$(1+K)\lambda = \frac{9}{8}\pi\left(\frac{1}{\beta R} + \frac{1}{\beta^2 R^2}\right) + q$$

where q is another constant equal to $\frac{p.r.T}{4}$. Substituting the value of K to be $\frac{1}{2} + \frac{9}{4\beta R}$ (according to Stokes) and rearranging the terms, we get the above equation reduced to the form :

$$\frac{4\lambda}{9\pi}\left(3 - \frac{q}{\lambda}\right)\beta^2 R^2 - \left(1 - \frac{2\lambda}{\pi}\right)\beta R - 1 = 0 \qquad \ldots \ (15)$$

This equation involves two unknowns β and q ; but as $\beta = \sqrt{\frac{\pi\rho}{\eta T}}$ it depends upon T and thus varies from stem to stem. Hence we write $a = R\sqrt{\frac{\pi\rho}{}}$

which will have the same value for all stems. βR is then equal to $\dfrac{a}{\sqrt{T}}$. Equation (15) may then be written down as :

$$\frac{4\lambda}{9\pi\tau}\left(3 - \frac{q}{4\lambda}\right)a^2 - \left(1 - \frac{2\lambda}{\pi}\right)\frac{a}{\sqrt{T}} - 1 = 0 \qquad \ldots \ (16)$$

As the experiment has been performed with 4 different stems, 4 such equations are obtained. From any two of the four equations, the values of a and q can be obtained. Taking the two equations corresponding to the stems A and C (given in Table III) and solving in the usual way, it is found that

$$a = 94.56$$

and

$$q = 0.1893$$

But since

$$a = R\sqrt{\frac{\pi\rho}{\eta}} \text{ , we get}$$

$$\eta = \frac{\pi\rho}{a^2} \cdot R^2$$

On substitution, η is obtained to be 0.00916.

As a test of the theory proposed : the above value of q is now substituted in the two remaining equations (corresponding to B and D) and η calculated from each one of them. The values thus obtained are found to be 0.00919 and 0.00911 in good agreement with the above value.

The values of η obtained here are however greater than the capillary flow value (0.008216) by about 10%. But for this reason it cannot be said that Stokes' theory is not valid. It is to be noted that this part of the experiment is not susceptible to as high an accuracy as the first part. The individual values of λ determined from successive experiment with the same stem differ from one another by even as much as 3% in some cases, and since μ is nearly proportional to λ^2 (Equation 12b) the error due to this cause alone may be 6%. Also since the correction applied for the stem depends upon the small differences in the value of η from stem to stem, the corrected value cannot have high accuracy when the uncorrected value of η has an error of even 1 or 2 per cent. In view of these considerations the value obtained for η in the experiment cannot be taken to be unsatisfactory. To the accuracy that the experiment is capable of giving we may consider that Stokes' theory in regard to damping is verified by this method.

We may therefore conclude that (i) Stokes's theory of a sphere oscillating in a fluid is quite valid both in regard to its virtual mass and the forces exerted on it due to the internal friction of the liquid.

(*ii*) The oscillating float offers a good method for investigating problems connected with the motion of solids in liquids, especially for determining their virtual mass.

(*iii*) Some light is thrown on the oscillations of a floating body itself, and the theory advanced in this paper, that the liquid surface exerts a damping force on a body moving through it will have to be further investigated.

In conclusion, I wish to offer my grateful thanks to Dr. J. Roy Strock, our Principal, for encouraging research work in our College, and Dr. I. Ramakrishna Rao of the University College, Waltair, for going through this paper and giving me valuable suggestions.

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ON THE THEORY OF SEMI-CONDUCTORS IN MAGNETIC FIELD

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ABSTRACT. The present paper investigates the theory of change of resistance of semi-conductors in magnetic field. In the first article of the paper a brief statement of Wilson's model of impurity semi-conductor is given. In the second and third articles general mathematical formulation of conductivity is derived taking into consideration Lorentz force only, for the models of Bloch and Nordheim. In the fourth article a general discussion of the foregoing results together with a critical resumé of Harding's paper on change of resistance of semi conductor is given. The difficulties of accepting Harding's paper *ipso facto* are indicated.

INTRODUCTION.

Generally accepted picture of free electrons in metals, was considered for a long time as the only satisfactory mode of attack on conduction problems. This classical concept of free conduction electrons as introduced by Drude and Lorentz played a most important role in the understanding of the mechanism of conduction, notwithstanding its serious drawbacks in explaining a number of experimental observations. The whole subject remained at this stage, for a considerable period, until this was revived by Sommerfeld,[1] who, following up broadly the old classical concept, most ingenuously introduced a Fermi-distribution of electron gas in place of Maxwellian. This modification, indeed put a new stimulus to a number of investigators, namely, Houston, Bloch, Nordheim and Peierls[2], who introduced new quantum mechanical concept into the subject and arrived at a more satisfactory and correlated understanding of mechanism of conduction. The phenomenon of Super-conductivity, however, remains still to be explained. Notwithstanding the brilliant work of the above mentioned workers in the line, a general and definite theory on conduction in magnetic field is yet to be welcomed. As for example it has been observed experimentally, particularly by Kapitza,[3] that the change of resistance in metals under magnetic field obeys a particular law. In a weak field, change of resistance obeys a square law and in a comparatively stronger field, a linear law. This may

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be assumed, however, that the two effects, one contributing to a square law and the other contributing to a linear law exist simultaneously, but in weaker field square effect is more pronounced up to a certain point and then makes a sudden transit to the linear law. Sommerfeld qualitatively explained this square effect in a comparatively weaker magnetic field but failed in the quantitative estimation of the constant of the square law and also could offer no explanation for the change of resistance obeying a linear law in a comparatively stronger magnetic field He also fails to give any account of temperature-dependence law. Frank,[4] however, extended Sommerfeld's calculation (on the assumption of free electrons) and obtained a rather complicated expression which provides for a quadratic law in a weak field but saturation follows in an extremely strong field instead of the linear law as observed. His theory also failed to give a correct estimation of the coefficient of the square law. Change of resistance in all the above cases was considered in a magnetic field transverse to the electric field and in no case the above investigators could put forward any explanation whatsoever, for the change of resistance when the magnetic field is parallel to the electric field. It has been experimentally observed that the change of resistance in the longitudinal field is of the same order as of that in a transverse magnetic field. Bloch,[5] however, tried to overcome this difficulty by assuming the effect of magnetic field in changing the direction of spin of the electrons. This change of orientation would cause a change in the velocity of electrons and thus resulting a change of resistance. Bloch also failed to obtain the right order of magnitude for the coefficient of square law and to explain linear law. Peierls[6] also carried out extensive investigations in this line from different standpoints and ultimately succeeded in explaining change of resistance both in parallel and transverse magnetic fields. He considered that frequency of collisions (in Bloch's model of electron gas where electrons move in a periodic potential field) in different directions are different and this anisotropy accounted for the change of resistance both in transverse and longitudinal fields. Here again Peierls failed to account for the linear law and obtained the saturation in strong magnetic field like Frank and also arrived at a quantitative agreement with the experimental results, in regard to square law coefficient, by taking an abnormally large anisotropy of τ (average time period between collision). The first successful attempt to correlate the experimental results so far available, with the theory was made by Titeica.[7] He introduced the quantisation effect under magnetic field and explained the change of resistance both in longitudinal and transverse fields. He also depicted correctly the linear law and found a quantitative agreement in the coefficient of the square law. This concept of quantisation, extending it to the problem of resistance in metals under very strong magnetic field was borrowed from Landau[8] who first considered this effect in explaining the diamagnetism in metals. Briefly, we may explain the quantisation effect qualitatively as follows: Normally, the electron under the influence of Lorentz's force does not describe

a complete orbit in consequence of its frequent encounterings with the ions. The electron may just describe small arcs of its orbit between successive collisions (indicating thereby a continual tendency of becoming quantised), *i.e.*, normally the time period of spiralling of an electron is very very much greater than that between two collisions. If on the other hand, the time period of spiralling is smaller than that between two collisions, the electron can freely describe its orbit without encountering another ion in its way. This orbital motion has its equivalence in two harmonic oscillators and thus in the language of new quantum-mechanics the energy intake of the electron in magnetic field is quantised. It is therefore apparent that there must be some critical value of the magnetic field at which the quantisation effect becomes pronounced and this critical value of magnetic field is given by $H_0 = \dfrac{mc}{e\tau}$, *i.e.*, the mean free path is of the order of radius of spiralling orbit.

In case of semi-conductors it has been experimentally observed that, in contrast to metals, the saturation is reached in the strong magnetic field after the square law (weak field). It could therefore be expected that the quantisation effect was non-existent in case of semi-conductors. On this assumption Harding [9] investigated quantitatively on Wilson's model,[10] the change of resistance in semi-conductors and found both qualitative and *quantitative* agreement with the observed results. It should be particularly noted that notwithstanding the fact that almost all investigators, in case of metals, succeeded in explaining the qualitative nature of the square law,—yet failed completely and definitely in quantitative confirmation· As for example, in case of alkali metals (inspite of the fact that all the data necessary for the quantitative evaluation of the change of resistance, are more or less accurately known) the discrepancy between the calculated and observed results is astonishingly large. Koretz[11] gave the following values :—

Metal	Change of Resistance	
	calculated	observed
Li ...	$5\cdot6 \times 10^{-7}$	$1\cdot5 \times 10^{-1}$
Na ...	$1\cdot1 \times 10^{-5}$	7×10^{-2}

It is therefore quite probable that one would accept Harding's results with a little hesitancy. It is proposed that in this paper we would endeavour to investigate the problem of the change of resistance of semi-conductors in magnetic field afresh from a different mathematical standpoint, though principally the same as Harding's, and confine ourselves only to the transverse

magnetic field.　It is proposed to continue this investigation further, in evaluating the change of resistance, incorporating the effect of quantisation both in transverse and longitudinal fields.

In the first part of this paper it is proposed to discuss very briefly the model of a semi-conductor as outlined by Wilson and Fowler.[10]　In the second part, a short mathematical formulation of the problem together with the important analysis will be presented.　In the third part, we shall apply the results as obtained in part II, to the particular case of impurity semi-conductors and work out the change in resistance both in weak and strong magnetic field. In the above calculations both the models (Bloch's and Nordheim's) will be taken into consideration.　The results will then be compared with the observations and a critical discussion will be given, on the strength of this comparison, as to the validity of the present theory on semi-conductors.

§1　MODEL.

Before entering into the mathematical formulation of the problem we may briefly discuss the models of metal and semi-conductor.　Metals may be considered as composed of atoms placed at a distance of lattice-constant from one another. The electrons in the atoms may be considered as confined in potential boxes, each box, however, having definite energy levels corresponding to the levels of the atom, and these energy levels are occupied by the electrons.　If we consider an isolated atom, these electrons in definite energy levels are bound to their respective levels.　The probability of any electron, to leak out of the box, is infinitesimally small.　Thus in such a case each one of the energy levels is sharply defined.　Now when we bring closer to this isolated atom other atoms (as in actual metal), the whole picture then changes and the probability of leakage of each electron increases.　As a direct consequence, no longer the energy levels remain sharply defined but they are broadened and in the potential box we have alternately allowed and forbidden zones, corresponding to the case of an isolated atom where allowed zone consisted of a sharp energy level.　The energy difference between the adjacent levels in the allowed zone is very very much smaller so as to form a continuous band (energy difference being of the order of a maximum of 5 electron-volts.)　The energy difference between a level in the allowed zone and the next higher level in the forbidden zone is enormous (the energy difference is of the order of 10^6 electron-volts).　Thus we see that all the electrons though bound in the classical sense, are now free to move through the lattice.　Now, as to which of these electrons will actually take part in conduction, will be decided by the Pauli's exclusion principle, which definitely fixes the number of electrons that can occupy any particular energy level.　When a particular level takes in as many number of electrons as is permissible according to this principle, the level is filled up or saturated and when there is a deficiency in the number of

electrons occupying any particular level, the level is partially filled or unsaturated. As the electrons usually (not applicable to rare earth and transition groups) saturate these levels successively starting from the lowest,—it is only the outermost level that remains unsaturated. The substance composed of atoms with saturated and unsaturated levels is a conductor and the electrons in the outer most unsaturated level take part in conduction; if however, all the levels are filled up (the substance is an insulator provided the outermost empty levels do not overlap as in the case of calcium). Now if the thermal agitation is sufficient enough to enable an electron to jump from one of the occupied level to the next higher unoccupied level, then under that circumstance the substance will behave as a conductor even if all the levels be normally filled up. It may be noted however, that in this particular case of conduction the temperature of the substance must have to be abnormally high (see Fowler). Under normal circumstances an insulator may, however, behave as a conductor when small traces of a foreign substance are introduced into it in the form of impurity such that the energy levels of this foreign substance lie just below unoccupied energy levels of the insulating substance. Due to the close proximity of the unoccupied energy levels of the insulating substance and the energy level of the foreign substance a small thermal agitation will be quite sufficient to remove an electron (as a process of thermal dissociation) from its own level to its next higher unfilled level. Thus we see that a number of conduction electrons is artificially created (so to speak) within the insulating substance. Since very small traces of the foreign substance are introduced, therefore, the concentration of electrons in the outermost level (hitherto unoccupied) will be very very low and the distribution of electrons is to be taken as Maxwellian. This particular model of semi-conductor is due to Wilson and Fowler and* we shall base all our calculations on this model. In our present paper we shall introduce both the prevalent lattice models in our general solution, namely, deformable ionic lattice (Bloch) in which it may be assumed that each ion is so displaced that it induces a continuous plane elastic Debye waves—whereas in the rigid ionic model (Nordheim), each ion may be considered to be rigidly fixed to the lattice and undisturbed by the action of elastic waves. It may be inferred, however, from the picture of the two models, that at lower temperature deformable model may prove more satisfactory whereas at higher temperatures (above Debye temperature) Nordheim's model may furnish better results. The object of incorporating both the models in our paper is to observe the relative correctness of the two models in our problem. (See the article by Bethe[12] where he advocates for Bloch's model and considers Nordheim's as absurd).

2. We shall now investigate the change in the distribution function of the electrons in the model semi-conductor as outlined above, subjected to external

* There are other cases of semi-conductors which shall not be discussed here. For detailed account see. reference (10)

electrical and magnetic fields, taking into consideration the interaction of the electrons with the lattice vibrations. It is then given by the well known Boltzman equation :—

$$\frac{\partial f}{\partial t}_{\text{(total)}} = \frac{\partial f}{\partial t}_{\text{(field)}} + \frac{\partial f}{\partial t}_{\text{(collision)}} \qquad \ldots \text{(1)}$$

whence $\qquad f = f_0 + f_1 \qquad$ and $\qquad f_1 << f_0 \qquad \ldots$ (2)

f_0 = distribution without field

f_1 = distribution in presence of field alone

$$f_0 = \frac{1}{\frac{1}{A}e^{E/kT} + 1} \qquad \ldots \text{(3)}$$

$$A = \frac{nh^3}{2(2\pi mkT)^{3/2}} = \text{the Sommerfeld's criterion}$$

for degeneracy $\qquad \ldots$ (4)

or introducing the time of relaxation as defined by

$$\left(\frac{\partial f}{\partial t}\right)_{\text{(collision)}} = -\frac{f_1}{\tau} \qquad \ldots \text{(5)}$$

we can write out the equation (1) as follows :—

$$\frac{\partial f}{\partial t} + \left(\overrightarrow{v} \operatorname{grad}_{\overrightarrow{r}} f\right) + \frac{1}{m}\left(\overrightarrow{F} \operatorname{grad}_{\overrightarrow{v}} f\right) + \frac{f_1}{\tau} = 0 \qquad \ldots \text{(6)}$$

$\overrightarrow{F}$ = Force acting on one electron

$$= e\overrightarrow{E} + \frac{e}{c}\left[\overrightarrow{v}\ \overrightarrow{H}\right] \qquad \ldots \text{(7)}$$

$\overrightarrow{E}$ and $\overrightarrow{H}$ are respectively the strengths of electric and magnetic fields,

For the solution of equation (6) let us put

$$f_1 = \left(\overrightarrow{\chi(E)}\ \overrightarrow{v}\right) \qquad \ldots \text{(8)}$$

$\overrightarrow{\chi(E)}$ is a vector depending on the magnitude of E.

Substituting (2) and (8) in equation (6) and introducing (3) equation (6) reduces, after some simple deductions to :

$$- \frac{\partial f_0}{\partial E} \, \tau \left\{ \frac{kT}{A} \left(\operatorname*{grad\,A}_{\tau} \right) + \frac{E}{T} \left(\operatorname*{grad\,T}_{\tau} \right) - e\vec{E} \right\}$$

$$+ \frac{e}{mc} \left[\vec{H} \, \vec{\chi} \right] \tau + \vec{\chi} = 0 \qquad \qquad \dots (9)$$

or putting in abridged form

$$\vec{M} = - \frac{\partial f_0}{\partial E} \, \tau \left\{ \frac{kT}{A} \left(\operatorname*{grad\,A}_{\tau} \right) + \frac{E}{T} \left(\operatorname*{grad\,T}_{\tau} \right) - e\,\vec{E} \right\} \qquad \dots (10)$$

$$\vec{N} = \frac{e\,\vec{H}}{mc} \tau \qquad \qquad \dots (11)$$

the equation (9) finally reduces to

$$\vec{\chi} + [\vec{N} \, \vec{\chi}] + \vec{M} = 0 \qquad \qquad \dots (12)$$

Solving (12), we obtain [13]

$$\vec{\chi} = - \frac{\left\{ \vec{M} + [\vec{N} \, \vec{M}] + \vec{N} (\vec{N} \, \vec{M}) \right\}}{1 + (\vec{N} \, \vec{N})} \qquad \dots (13)$$

Having solved $\vec{\chi}$, we may at once proceed to calculate the currrent and thence the conductivity. The current is given by :

$$\vec{i} = 2e \int_0^\infty f_1 \, \vec{v} \, d\Omega \qquad \qquad \dots (14)$$

$$d\Omega = \frac{m^3}{h^3} dv_x \, dv_y \, dv_z \qquad \qquad \dots (15)$$

or $\qquad \vec{i} = \frac{2\,e\,m^3}{h^3} \iiint \vec{v} \left(\vec{v} \, \vec{\chi} \right) dv_x \, dv_y \, dv_z \qquad \dots (16)$

Assuming the material to be homogeneous and the temperature constant throughout the material and with the help of (16), (13), (10) and (11), we may easily arrive at an expression for the current in the x-direction as follows :—

$$i_x = -\frac{2 e^2 m^3}{h^3}\left\{ E_r\, K\, +\, \frac{c}{mc}\left[\vec{H}\,\vec{E}\right]_x L + H_x\left(\vec{H}\,\vec{E}\right)P\right\} \qquad \dots\ (17)$$

where

$$K = \iiint \frac{v_x^2\, \tau\, \frac{\partial f_0}{\partial E}\, dv_x\, dv_y\, dv_z}{1 + e^2\, \tau^2\, H^2/m^2 c^2} \qquad \dots\ (18)$$

$$L = \iiint \frac{v_x^2\, \tau^2\, \frac{\partial f_0}{\partial E}\, dv_x\, dv_y\, dv_z}{1 + e^2\, \tau^2\, H^2/m^2\, c^2} \qquad \dots\ (19)$$

$$P = \iiint \frac{v_x^2\, \tau^3\, \frac{\partial f_0}{\partial E}\, dv_x\, dv_y\, dv_z}{1 + e^2\, \tau^2\, H^2/m^2 c^2} \qquad \dots\ (20)$$

3. Let us now proceed to investigate the conductivity in a transverse magnetic field, *i.e.*, the magnetic field is applied in the z-direction when the impressed electric field is in the x-direction.

We therefore obtain :

$$i_x = -2\,\frac{e^2 m^3}{h^3}\left\{ E_x\, K\, -\, H_z\, E_y\, \frac{c}{m c}\, L\right\} \qquad \dots\ (21)$$

$$i_y = -2\,\frac{e^2 m^3}{h^3}\left\{ E_y\, K\, +\, H_z\, E_x\, \frac{c}{m c}\, L\right\} \qquad \dots\ (22)$$

$$i_z = 0 \qquad \dots\ (23)$$

Transverse electric field in the y-direction is due to Hall effect and to prevent the flow of the Hall current, we must substitute a field E_y in opposition.

And therefore to make $i_y = 0$, we obtain from (22)

$$E_y = -\frac{c}{m c}\, \frac{L}{K}\, H_z\, E_x. \qquad \dots\ (24)$$

Substituting the value of E_x from (24) in (21) we obtain the expression for the conductivity in the x-direction as follows :—

$$\sigma_x = - \frac{2e^2 m^3}{h^3} \left\{ K + \frac{L^2}{K} \frac{e^2}{m^2 c^2} H_z^2 \right\} \qquad \ldots \ (25)$$

Now for the evaluation of the conductivity, a knowledge of the values of the integrals K and L as given by (18) and (19) is essential. General evaluation of these integrals are not possible and we therefore restrict ourselves to the two limiting cases of the problem :

$$
\left.
\begin{array}{ll}
(i) & H <\!< H_0 ; \quad H_0 = \dfrac{mc}{e\tau} \\[1ex]
& \textit{i.e., when magnetic field is weak}
\end{array}
\right\} \qquad \ldots \ (26)
$$

(ii) $H >\!> H_0$, *i.e.*, when the magnetic field is strong.

As explained in § 1, $H = \frac{mc}{c\tau} = H_0$, will mean physically that the magnetic field is such as to cause the spiralling of the electron round the magnetic field as axis, the spiralling effect thus playing an important role when $H >\!> H_0$.

Further we may take the time of relaxation $\tau^{[14]}$ from either of the models of Bloch or Nordheim

$$\tau_{\text{(Bloch)}} = \frac{C_n}{E^{1/2}} \quad \text{where} \quad C_n = \frac{3^{4/3} \ \pi^{2/3} \ (k\theta)^2 \beta^{3/2} \ da^5}{2^{2/3} \ h \ kTC_1^2} \qquad \ldots \ (27)$$

(θ = Debye temperature.
δ = density.
a = lattice constant.
β = a constant depending on the lattice structure.
κ = Boltzmann constant.

and $\qquad C_1 = \dfrac{n^2}{8\pi^2 m} \displaystyle\int \left| \text{grad. } U_k \right|^2 d\tau \qquad$ =average kinetic energy of the electron)

From Nordheim's model :

$$\tau_{\text{(Nordheim)}} = C_N E^{3/2} ; \quad \text{and} \quad C_N = \frac{2^{5/6} \ (k\theta)^2 a^8 m^{1/2} \ d}{3^{2/3} \ \pi^{1/3} \ Z^2 e^4 h^2 kTJ} \qquad \ldots \ (28)$$

where $J = \frac{1}{2}\left[\log_e (t+1) - \frac{t}{t+1} \right]$, and $t = 1 \cdot 36.10^{12} b^2 T$ $\qquad \ldots \ (29)$

b = screening constant.

(For notations see reference 14).

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Let us now investigate the case when $H \ll \frac{mc}{e\tau}$, and τ is given by the Bloch's model [(*i.e.*, from (27)], whence we obtain after integration—

$$K = -C_B A 4/3 \; \pi \; \frac{2^{3/2}}{m^{5/2}} \; kT \left(1 - \frac{C_B^2 \; e^2 H^2}{m^2 c^2 kT} \right) \qquad \ldots \; (30)$$

$$L = -C_B^2 \; A \; \frac{2}{3} \; (2\pi)^{3/2} \; \frac{1}{m^{5/2}} \left(kT \right)^2 \left(1 - \frac{2C_B^~ \; e^2 H^2}{m^2 c^2 kT} \right) \qquad \ldots \; (31)$$

Where as taking τ for Nordheim's model from (28) :

$$K = -C_N A \frac{4}{3} \; \pi \; \frac{2^{3/2}}{m^{5/2}} . 2.3 \; (kT)^3 \left\{ 1 - \frac{C_N^2 \; .120 e^2 H^2 \; (kT)^3}{m^2 c^2} \right\} \qquad \ldots \; (32)$$

$$L = -C_N^2 \; A \frac{4}{3} \; \pi^{\frac{3}{2}} \frac{2^{3/2}}{m^{5/2}} . \frac{945}{32} (kT)^{9/2} \left\{ 1 - \frac{2145}{8} . C_N^2 \; \frac{e^2 H^2}{m^2 c^2} . (kT)^3 \right\} \qquad \ldots \; (33)$$

For the limiting case of a strong field, *i.e.*, when $H \gg \frac{mc}{e\tau}$ and considering τ from Bloch's model we have :

$$K = - \frac{A}{C_B} \; \frac{4}{3} \; \pi \; \frac{2^{5/2}}{m^{5/2}} (kT)^2 \; \frac{m^2 c^2}{e^2} \; \frac{1}{H^2} \qquad \ldots \; (34)$$

$$L = -A . \pi^{3/2} \; \frac{2^{3/2}}{m^{5/2}} \; (kT)^{\frac{3}{2}} \; \frac{m^2 c^2}{e^2} \; \frac{1}{H^2} \qquad \ldots \; (35)$$

and for the same strong magnetic field taking into consideration τ for Nordheim's model, we have :

$$K = - \frac{A}{C_N} \; \frac{4}{3} \; \pi \; \frac{2^{3/2}}{m^{5/2}} \; \frac{m^2 c^2}{e^2} \; \frac{1}{H^2} \qquad \ldots \; (36)$$

$$L = -A \; \pi^{3/2} \; \frac{2^{3/2}}{m^{5/2}} (kT)^{3/2} \; \frac{m^2 c^2}{e^2} \; \frac{1}{H^2} \qquad \text{(same as Bloch's)} \qquad \ldots \; (37)$$

With the above values of integral substituted in the equation (25) we get the change in conductivity as follows :—

For weak field.

$$\frac{\Delta\sigma}{\sigma_0} = \frac{C_P^2 e^2}{m^2 c^2 kT}\left(\frac{\pi}{4} - 1\right)H^2 \qquad \text{(Bloch)} \qquad \dots \text{(38)}$$

$$\frac{\Delta\sigma}{\sigma_0} = \frac{C_N^2 e^2}{m^2 c^2}\, 44(kT)^3\, H^2 \qquad \text{(Nordheim)} \qquad \dots \text{(39)}$$

Where σ_0 is the conductivity in the absence of the magnetic field.
If we express the results in terms of resistance we get :

$$\frac{\Delta R}{R} = \alpha H^2 \qquad \dots \text{(40)}$$

For Bloch's model—

$$\alpha_{\text{(Bloch)}} = 0.22\left[\left(\frac{8\text{I}}{32\pi}\right)^{2/3}\left(\frac{2\pi c^2}{hc}\right)^2 \frac{k}{e^2 m^2} \cdot \frac{\beta^3 \theta^4 d^2 a^{10}}{C_1^3 T^3}\right] \qquad \dots \text{(41)}$$

$$= 7.44 . 10^{51}\, \frac{\beta^3 \theta^4 d^2 a^{10}}{C_1^3 T^3} \qquad \dots \text{(42)}$$

and for Nordheim's model

$$\alpha_{\text{(Nordheim)}} = \frac{44.2^{5/3}}{mc^2 3^{4/3}}\frac{k^5}{\pi^{2/3}}\frac{1}{e^6 h^4} \blacksquare \frac{\theta^4 a^{16} d^2 T}{z^4 J^2} \qquad \dots \text{(43)}$$

$$= 4.11 . 10^{88}\, \frac{\theta^4 a^{16} d^2 T}{z^4 J^2} \qquad \dots \text{(44)}$$

For the limiting case of a strong field

we obtain :—

$$\frac{\Delta R}{R(H \to \infty)} = 0.117 \qquad \text{(Bloch)} \qquad \dots \text{(45)}$$

$$\frac{\Delta R}{R(H \to \infty)} = 0.705 \qquad \text{(Nordheim)} \qquad \dots \text{(46)}$$

It should be particularly and most emphatically pointed out that for the evaluation of change of resistance, and to arrive at a quantitative agreement with the experimental results, we are faced with a number of variables whose values

are not definitely known yet. As for example, it is quite apparent from the equations (42) and (44) that the proportionality factor a is very sensitive to the quantities which entirely depend on a definite knowledge of the structure of the crystals concerned and unfortunately the values of such quantities could only be fixed very approximately. In our case any significant variation in the value of the lattice constant shall introduce an appreciable change in the final calculations. We, however, proceed to make a quantitative estimation of the proportionality factor α with reasonable values for the above quantities.

Taking the case for germanium—

$$\theta = 2 \cdot 10^2 \text{ Abs.*}$$

$$d = 5 \cdot 46 \text{ grams/cm}^3,$$

$$T = 3 \cdot 10^2 \text{ Abs.}$$

$$C_1 = 1 \cdot 8 . 10^{-11} \text{ ergs.}$$

$$\beta = 1 \cdot 6 . 10^{-12} \text{ ergs.}$$

$$a = 5 \cdot 9 . 10^{-8} \text{ cm*}$$

$$v = 4 \times 10^5 \text{ cm/second.}$$

We obtain on substitution of above values

$$\frac{\Delta R}{R} \simeq 2 \cdot 62 . 10^{-10} \text{ H}^2 \quad \text{(Bloch.)} \qquad\qquad\qquad \text{(47)}$$

$$\frac{\Delta R}{R} \simeq 2 \cdot 2 \times 10^{-12} \text{H}^2 \quad \text{for,} \quad b = \frac{a}{2} \left.\begin{array}{c} \\ \\ \end{array}\right\} \quad \text{(Nordheim)} \qquad \text{...} \quad \text{(48 and 49)}$$

$$\simeq 1 \cdot 115 \times 10^{-8} \text{H}^2 \quad \text{for} \quad b = \frac{a}{6}$$

We thus find that in both the models theoretical estimation is in reasonable agreement with the observations of Kapitza. But as stated above, the agreement may only be accepted with reservation, since the result may vary to a large extent with the slightest change in the Debye temperature or in the lattice constant. We

---

* Using the formula $\theta \sim 5 \cdot 5 \ 10 \frac{{}^3 d^{1/2}}{A}$, Abs—(see Electronen theorie der Metalle, p. 272, H, Frolich) where A = atomic weight, we obtain $\theta \sim 177°$ Abs.—thus a value of the order of 200 Abs may be taken reasonably. The lattice constant " a " is then calculated from the relation

$$k\theta = \frac{hv}{a} \left(\frac{3}{4\pi} \right)^{\frac{1}{3}} \qquad\qquad \text{...} \quad \text{(B)}$$

also find here that Bloch's model furnishes us with correct relationship between the change of resistance and temperature whilst Nordheim's model fails to do so. In our problem it may be asserted that Nordheim's model is unsatisfactory notwithstanding the fact that in the limiting case $H \to \infty$ both the models give values for $\frac{\Delta R}{R}$, which are approximately of the same order of magnitude, and also furnish with reasonable quantitative agreement for α. Let us now compare our results with those obtained by Harding who claims to have a quantitative agreement with the experimental results. But as revealed in the foregoing discussion, firstly there is an error of the order of 256 in Harding's calculation for $\frac{\Delta R}{R}$ and secondly Harding presumably takes an abnormal Debye temperature $\theta \sim 1180^\circ$ Abs.[*] Harding's result, when corrected, comes out as follows :—

$$\frac{\Delta R}{R} \sim 6 \cdot 2 \times 10^{-15} H^2 \qquad \dots \quad (50)$$

Thus we observe that the calculated results do not rigorously corroborate the observed fact, We shall now leave aside rigid ionic model (Nordheim) in the evaluation of Hall constant as it fails to give the important relationship of change of resistance with temperature although we arrive at a nearer quantitative agreement for the coefficient α than that given by Bloch.

Hall constant is defined by :

$$R_{\scriptstyle\rm H} = \frac{E_y}{i_x H} = -\frac{e}{mc}\,\frac{L}{k}\,\frac{1}{\sigma_{\rm H}} \qquad \dots \quad (51)$$

For weak field

$$\frac{R_{\scriptstyle\rm H}}{R_0} = \left(1 - 0 \cdot 78\, \frac{C_3^2 c^2}{m^2 c^2 kT} \cdot H^2 \right) \dots \text{(Bloch)}$$

$$\sim (1 - 9 \cdot 3 \times 10^{-10} H^2) \qquad \dots \quad (52)$$

For strong field, $H \to \infty$

$$\frac{R_{\scriptstyle\rm H}}{R_0} = 0 \cdot 848 \qquad \text{(Bloch)} \qquad \dots \quad (53)$$

[*] Harding takes $a \sim 10^{-8}$ cm. and $v = 4 \cdot 10^5$ cms/sec. and θ comes out immediately from the relationship (B) in the previous footnote.

CONCLUSION.

From the foregoing results and discussion we are of opinion that the theory of semi-conductors in magnetic field under the assumption of Lorentz force only is to be accepted with reservation. Although the nature of the experimental curve for change of resistance in the magnetic field (in weak field the change is proportional to H^2, followed by a saturation in strong field), yet the quantitative agreement can only be arrived at under circumstances (by adjusting the variables as indicated in the paper), which are not altogether free from a certain amount of reasonable suspicion. It will be, however, interesting to investigate experimentally the change of resistance of semi-conductors in a longitudinal magnetic field, which alone can definitely decide whether quantisation has any effect in our particular problem.

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A NOTE ON THE δ (CH) VIBRATION IN SODIUM FORMATE.

BY JAGANNATH GUPTA.

Plate XII.

ABSTRACT The composite character of the Raman line 1398 cm⁻¹ of formic acid is discussed, in contrast with the line 1353 cm⁻¹ of sodium formate, from points of view of nature, intensity and polarisation characters. Spectrograms are reproduced to show that the 1398 line of formic acid is replaced by a pair of lines, 1355 and 1395, of different intensities, in the crystals of sodium formate The feeble intensity of the line 1395, which is identified with the δ (CH) vibration of the formate ion, is in accord with the intensity of the corresponding line in other organic molecules where a single hydrogen atom is attached to carbon.

The Raman line $\Delta \nu$ 1398 of formic acid, which is usually attributed to the deformation oscillation of (C − H), is broad, moderately intense, and has a depolarisation factor 0·41. This value is unexpected, since the value of ρ of the corresponding line in the various other aliphatic compounds [1] like the acids, alcohols, esters, ketones, alkyl halides, etc., very nearly approaches 6/7,—the ideal value for total depolarisation.

The line 1353 of sodium formate (examined in aqueous solutions) is, on the contrary, exceedingly sharp and intense, and polarised to a great extent $(\rho = \cdot 17)$.[2] The attribution of this line to the δ (CH) vibration is associated with even greater difficulties, considering its polarisation character. Moreover, since the line 1353 is by far the most intense Raman line in the spectrum of sodium formate,[3] such an attribution leads to the conclusion that in the formate ion, the deformation oscillation of the hydrogen atom against carbon gives rise to a more intense Raman line (1353 cm⁻¹) than the valence oscillation of the same (2834, 2736 cms⁻¹), which is to a high degree, improbable.

It was therefore suggested by the present author that the line 1353 of sodium formate has its origin in the symmetrical vibration of the ionised carboxyl group $\left(-C \diagup{}^{O}_{\diagdown O} \right)$, the thick lines representing the bond of resonance which is different from either the purely single or the double bond in its energy content. The point has been discussed in several subsequent communications,[4] with other molecules containing the carboxyl group.

The different degrees of depolarisation of the line 1398 of formic acid and 1353 of sodium formate (in solution) clearly point out that they are not of the

same origin. The 1398 line was therefore suggested to be a composite line, [3] arising from an accidental coincidence of the deformation vibration frequency of (C−H) and an inner vibration of the carboxyl.[5] Experimental evidences in favour of this explanation were its broad character and the departure of its value of ρ from 6/7.

It is obvious that no better evidence of its composite nature can be adduced than by actually resolving it into its components. Such an evidence is difficult to obtain from a spectrum of the formate in solution, where although one of the components (1353) is extremely intense, the other component (1375) (1385-Edsall [6]), is exceedingly feeble, and could not be recorded with sufficient intensities.

In the crystalline state, therefore, where Ray and Sarkar [7] postulate a a stronger force of binding between carbon and hydrogen than in solutions, an attempt has been made to see if the deformation vibration is recorded as a Raman line of reproducible intensity and separated from the symmetrical vibration of the ionised carboxyl under the influence of strong "crystalline" forces.

Nearly a gramme of the formate was obtained in small transparent crystals by slow crystallisation. The crystals were illuminated by the powerful radiation Hg 4047Å with the help of a pair of filters,—a very dilute solution of sodium nitrite to cut off 3650Å group of lines, and a concentrated solution of iodine in carbon tetrachloride to cut off 4358Å group of lines and others of longer wavelengths,—placed in the incident radiation from a quartz mercury arc. A saturated solution of sodium nitrite (10 mm. layer) was used as a complementary filter[8] in the scattered radiation. The spectrogram is reproduced in plate XII, with that of pure formic acid taken for comparison on the same variety of photographic plate (Ilford's Golden Isozenith), in the same spectrograph and with identical width of slit.

In the spectrum of solid sodium formate, the line 1398 of formic acid is clearly replaced by two lines 1350 and 1395. The sharp and intense line 1350 originates presumably from the symmetrical inner oscillation of the ionised carboxyl, while the faint companion at 1395 to the deformation oscillation of hydrogen in the formate ion, whose small intensity is in accordance with the feeble intensity of the Raman line attributed to the δ (CH) vibration in all organic compounds where a single hydrogen atom is attached to carbon in the molecule, e.g., in $CHCl_3$, $Cl_3C \cdot CHCl_2$, $CHBr_3$, $Cl_3C \cdot CHO$, $Cl_3C \cdot CH(OH)_2$, $Cl_2C=CHCl$ etc.
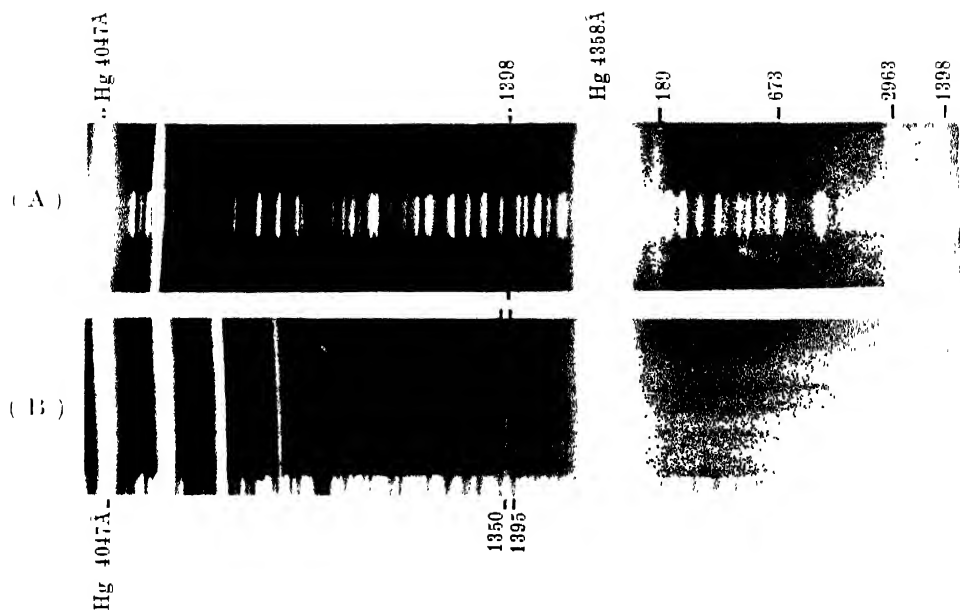
Raman Spectra.

(A) Pure formic acid
(B) Sodium formate crystal showing doublet at

$$\Delta \nu \ 1350 \ \text{and} \ 1395 \ \text{cm}^{-1}.$$

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TECHNIQUE FOR MAKING COLLODION FILTER FOR THE Kα CHROMIUM RADIATION.

BY SURAIN SINGH SIDHU, M.Sc , Ph.D.

ABSTRACT—Collodion filters of ammonium (meta) vanadate have been found very satisfactory in the obtaining of the Kα chromium radiation. This note describes the method of preparation, the concentration of vanadium which proved most suitable, and the satisfactory condition of operation of an X-ray tube in conjunction with such filters.

The methods for preparing the filters to obtain a monochromatic x-ray beam for purposes of crystal structure analysis, so far proposed, fall into two groups. If the filter element is in the form of a thin sheet, as for example, nickel foil for copper radiation, it is cut to the desired thickness and used as a filter. When the filter element is not obtainable in the above form however, as for example, vanadium, suitable filtering screens are made from a compound of the filtering element by one of the several ways. A filter paper may be soaked in the solution of a compound of the filtering element and dried; a compound of the filtering element may be mixed with another element of low atomic number and then spread on a sheet of paper coated with shellac; an element may be electro-deposited on an aluminium foil, as for example, manganese on aluminium for filtering iron radiation; and finally a compound of the filtering element may be suspended either in a paraffin block which may afterwards be cut to the desired thickness, or in collodion, which may be spread out in a thin sheet and allowed to dry.

Collodion filters of ammonium (meta) vanadate were prepared [1] by the latter method and have been found very satisfactory in the obtaining of the Kα chromium radiation. The method[2] of preparation, the concentration of vanadium which proved most suitable, and the satisfactory condition of operation of an x-ray tube in conjunction with such filters, are described below.

Mix 25 grams of well-powdered ammonium (meta) vanadate of technical grade $\{NH_4 VO_3, V$ (as V_2O_5) 77.05 ; Fe_2O_3 0.025; SiO_2 0.05; Cl 0.10; SO_3 0.01 ; alkali $0.16\}$ with 40 c.c. of collodion of the flexible variety[3] (24 per cent. alcohol, 72 per cent. ether) and 20 c.c. of 95 per cent. alcohol, and stir thoroughly.

Prepare several polished aluminium plates of $1'' \times \frac{1}{2}''$ size and half that many pieces of blotter of the same size. Take one of the plates and dip it into

the mixture, remove, allow to dry for a few seconds, turn it around and dip it again so that the end that formerly entered the liquid first, now enters last. Repeat the dipping until the desired thickness has been obtained. Set the coated plate aside. Treat the other plates the same way.

In less than an hour the coating will dry and peel off the plates. Put the coatings into a flat dish with alcohol in it. The alcohol will soften the coatings so that they can be spread out perfectly flat. Place a blotter on a plate and a coating on a blotter. Be sure that the coating is perfectly flat. Place another plate on the coating, clamp the whole assemblage and place it in an oven. Heat at about 80°C for half an hour to drive alcohol and ether out of the coating into the blotter. The coatings thus treated are the filters in the finished form. Cut the filter to the desired size with a razor blade.

To obtain the required temperature of 80°C an inexpensive oven was made from a stove pipe of 7 inches diameter and one foot length. One end of the pipe was tightly closed with a wooden base at the centre of which was screwed a lamp socket. The wires for the electrical connections to the socket were brought in through a narrow hole in the pipe near the base The other end of the pipe was covered with a wooden top to which was attached a metal shelf for supporting the assemblages. The shelf was about 7 inches from the bottom of the oven. A hole was made through the middle of the top for the insertion of a thermometer. The outside of the pipe was covered with a thick asbestos covering.

When a 75 watt Mazda lamp was connected to the socket and operated at normal voltage, it heated the oven to the desired temperature in half an hour.

Collodion filters of 0.5 to 0.6 mm. thickness were used in making powder photograms of pyrrhotite with the K_a chromium radiation, which was supplied by a Phillip's type demountable x-ray tube equipped with an aluminium window of 0.0005 inch thickness. The tube was operated at 40 K.V. peak and the load current was 20 milliamperes.

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AN APPLICATION OF THE RAY-DISPLACEMENT REFRAC-TOMETER· TO THE STUDY OF THE ANOMALOUS DISPERSION OF DIDYMIUM GLASS. *

By K. PROSAD

AND

R. P. GUPTA.

(Physics Department, Patna Science College.)

ABSTRACT. The paper deals with the application of the ray-displacement refracto-meter constructed by the authors and described some time back in this journal, to the study of the anomalous dispersion of a sample of didymium glass. The accuracy of measurements claimed for this instrument has been fully substantiated by the location of positions of absorption bands of didymium glass, known from previous measurements. Further, the study has un-mistakably located positions of other bands which photography had failed to reveal

1. INTRODUCTION.

In a paper [1] recently published in this journal, we had described a refracto-meter of a simple design but possessing considerable accuracy and had given the results of measurements of refractive indices of some solids and liquids with respect to a few wave-lengths

The object of this paper is to testify further to the accuracy and reliability of the apparatus, by studying the anomalous dispersion of a specimen of didymium glass whose absorption bands had been previously studied by one of us and described elsewhere [2]

2. EXPERIMENTAL.

The didymium glass was in the form of a cube about 1·3 cm. each way. Its exact composition was not known and was found in the laboratory in one of the old boxes in the storeroom. The apparatus having been assembled as described in our paper (*loc. cit.*), light from sodium lamp and each of the discharge tubes, namely, of hydrogen, neon, argon, krypton and helium, was used in succession, to determine the refractive indices of the glass with respect to as many as 26 lines distributed over the visible region of the spectrum, and found suitable for visual observation.

3. RESULTS.

The refractive indices calculated with the help of the formula—

$$\mu = \frac{\sin i}{t. \sin i - d} . \sqrt{d^2 + t^2 - 2\, d.t \sin i}$$

are given in table I with their corresponding wave-lengths and figure 1 is the dispersion curve obtained by plotting the tabulated vales of refractive indices against the wave-lengths used.

TABLE 1.

No. of obs.	Wave length in A. U.	Refractive index (Cal.).	Source.
1	4157	1·52222	Argon
2	4200	1 52518	Argon
3	4273	1 52424	Krypton
4	4318	1·52354	Krypton
5	4502	1·52648	Krypton
6	4628	1·52506	Argon
7	4702	1·52332	Argon
8	4861	1·52727	Argon
9	5162	1·52594	Argon
10	5221	1 52503	Argon
11	5280	1·52590	Neon
12	5400	1·52518	Neon
13	5562	1·52315	Krypton
14	5871	1 5232	Krypton
15	5893	1·52220	Sodium
16	6032	1·52144	Argon
17	6056	1·5205	Krypton
18	6143	1·52106	Neon
19	6266	1·52025	Neon
20	6383	1·51995	Neon
21	6402	1·51973	Neon
22	6416	1·52025	Argon
23	6421	1·51982	Krypton
24	6563	1·51820	Hydrogen
25	6599	1·51917	Neon
26	6678	1·51870	Neon

4. DISCUSSION.

Looking at figure 1 it will be found that bold lines have been drawn at six wave-lengths, namely 4714 Å, 4844 Å, 5126 Å, 5265 Å, 5786 Å and 5842 Å. These represent wave-lengths of absorption bands of the didymium glass found by one of us.[3] The well known feature of the dispersion curve bending in opposite directions across any absorption band due to 'anomalous dispersion' is very strikingly shown by the results of observations plotted here. It will be further seen from an inspection of figure 1 that local nature of bending of the dispersion curve in different regions points to the existence clearly of at least eleven absorption bands, six of which as pointed out earlier, have been actually observed by one of us. Two of the remaining five bands, namely those suggested from the curve at wave-lengths, 4180 Å and 4440 Å are in excellent agreement with the observation of Liveing and Dewar,[4] inspite of the fact that they worked with water solution in which the bands will be slightly shifted. Partly on account of the insensitiveness of the eye to light in this region and partly also to the absence of suitable wave-lengths closer to the absorption bands, a larger number of observations could not be taken to fix the positions of the absorption bands more closely. The above agreements in the values of wave-lengths of absorption bands indicated by the curve from the nature of the breaks, lend very strong support to the undoubted existence of absorption bands also at the three wave-lengths 6100 Å, 6407 Å and 6580 Å. In these regions the observations have gone much closer to the positions of absorption bands as will be seen from figure 1 and the bending of the dispersion curve in opposite directions is unmistakably clear.
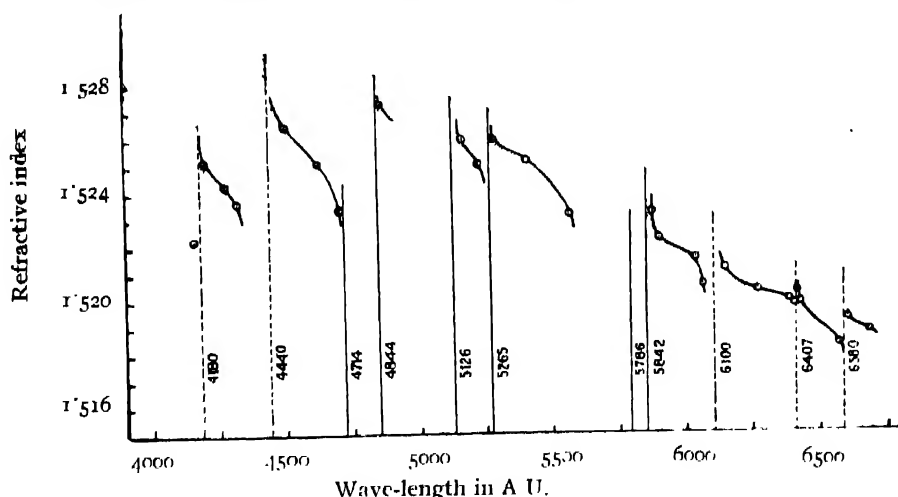

FIGURE 1.

It is interesting to point out here that a photograph of the absorption bands of the didymium glass taken with a Hilger constant deviation glass Spectro-

graph, records only the six bands studied by one of us. Neither the bands on the more refrangible side of 4714 Å nor those on the less refrangible side of 5842 Å make their appearance on the negative, so that using an instrument of the type pointed out above, to locate the positions of absorption band of didymium glass one is sure to miss them. The reason for this may be the small dispersion of the spectrograph in the red and the general absorption in the violet portion which didymium glass is well known to possess. The superiority of the ray-displacement refractometer in clearly locating positions of absorption bands many of which might be missed by ordinary methods of photography, is then unquestionable.

Lastly, using the well known electron theory of dispersion due to Lorentz and the values of refractive indices close to absorption bands as determined by us and recorded in this paper, it is possible to calculate roughly the values of the constants N_1, N_2, N_3, etc. in the equation—

$$\mu^2 = 1 + \frac{N_1 \cdot e^2}{\pi m_0 (\nu_1{}^2 - \nu^2)} + \frac{N_2 \cdot e^2}{\pi m_0 (\nu_2{}^2 - \nu^2)} + \dots \dots$$

These come out roughly to be—

$N_1 = 1.93 \times 10^{14}$	corresponding to band at	6580 Å
$N_2 = 0.71 \times$,,	,, ,, ,, ,, ,,	6407 Å
$N_3 = 5.84 \times$,,	,, ,, ,, ,, ,,	6100 Å
$N_4 = 11.29 \times$,,	,, ,, ,, ,, ,,	5842 Å
$N_5 = 3.57 \times$,,	,, ,, ,, ,, ,,	5265 Å
$N_6 = 9.92 \times$,,	,, ,, ,, ,, ,,	5126 Å

and appear to be of the correct order.

A more accurate determination was not possible as in many cases suitable lines for observation very close to the absorption bands were not available from any of the sources at our disposal.

In conclusion we would like to thank Mr. B N. Ghosh for help in calculation and Mr. S. N. Chatterjee for drawing the curve.

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ON THE INTENSITIES OF RAMAN LINES DUE TO LATTICE OSCILLATIONS.*

By S. C. SIRKAR.

PLATE XIII.

ABSTRACT. It is pointed out that the results of investigation of the Raman spectra of ammonium halides at different temperatures by Menzies and Mills definitely show that the Raman line due to lattice oscillation cannot have any appreciable intensity when the arrangement of the cations on opposite sides of an anion is symmetric. The arrangement of the molecules in the crystals of naphthalene, *p*-dichlorobenzene and *p*-dibromobenzene is discussed and it is shown that in these cases and especially in the case of naphthalene there cannot be any asymmetry in the arrangement of the two molecules on opposite sides of any particular molecule, and therefore the Raman line due to lattice oscillation cannot have any appreciable intensity in these cases. The Raman spectra of these crystals are reproduced to show the large intensities of the new lines close to the Rayleigh line relative to those of the other Raman lines. The above facts lead to the conclusion that the new Raman lines are due to oscillations in polymerised group as suggested previously.

INTRODUCTION.

It has been proved by the investigations of Rasetti[1] that lattice oscillations in ionic crystals of NaCl type can produce small changes in polarisability so that the corresponding Raman lines have appreciable intensities. In the case of calcite and aragonite also, a few moderately intense Raman lines are observed besides those due to the "inner" vibrations of the complex anion, and the origin of these extra lines have been attributed by Bhagavantam[2] to lattice oscillations. It was observed by Gross and Vuks[3] that in the spectra of light scattered by some organic crystals, *viz.*, naphthalene, diphenyl ether, *p*-dichlorobenzene and *p*-dibromobenzene, there are a few new Raman lines close to the Rayleigh line and it was suggested by the said authors that these lines also might be due to lattice oscillations. Such new lines have also been observed by the present author[4] in the case of many organic compounds in the solid state, having simple molecules, *viz.*, CS_2, CCl_4, $CHCl_3$, etc., and for various reasons it has been suggested[5] that these new Raman lines are probably due to oscillations in polymerised groups of molecules. It has been pointed out more recently by the present author and Gupta[6] that the

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* Read before the Indian Physical Society on the 27th September, 1937.

Z

abnormally high intensity of one of these new lines observed in the case of solid carbon disulphide precludes the possibility of its origin being in lattice oscillations, because a lattice oscillation cannot produce a change in polarisability greater than that due to the "breathing" oscillation of the molecule, and actually it is observed that the new line at 70 cm^{-1} is at least three times more intense than the line 655 cm^{-1} due to the breathing vibration of the carbon disulphide molecule.

Very recently, Venkateswaran[7] has remarked in a discussion that lattice oscillations can produce intense Raman lines and he has cited the example of diamond in support of his statement and has also remarked that the lines close to the Rayleigh line are due to lattice oscillations.

The oscillation in diamond lattice, however, is quite different from the lattice oscillation mentioned above, beause in the former case each carbon atom is linked to its neighbours by C—C bonds and any oscillation of the lattice entails either deformation or contraction of one or other of these bonds, and in the latter case no such linkage is taken into account unless one assumes the existence of polymerised groups in the crystal.

Also, it cannot be proved by citing the example of diamond that lattice oscillations can produce changes in polarisability much greater than that produced by the breathing oscillation of the molecule. The arguments put forward by Venkateswaran in support of the hypothesis that the new lines close to the Rayleigh line observed in the case of some organic crystals have their origin in lattice oscillations are, therefore, not very convincing.

There is experimental evidence, however, to show that even in the case of an ionic crystal, the Raman line due to lattice oscillation does not possess any appreciable intensity unless the arrangement of the ions is such that during the oscillation of the lattice there is an asymmetric restoring force. It has been observed, for instance, by Menzies and Mills[8] that a strong new line appears in the Raman spectrum of crystals of ammonium chloride at about -30°C., but no such line is observed in the case of NH_4Br. This difference in the behaviour of the two crystals has been explained by these authors by assuming that the arrangement of the NH_4 ions on opposite sides of a chlorine ion is asymmetric and that on the opposite sides of the bromine ion is symmetric. It is the purpose of the present paper to discuss particular cases of organic crystals of known structure in order to ascertain whether there may be any asymmetric restoring force during oscillations of the lattice and whether Raman lines due to lattice oscillations may have any appreciable intensity in these cases.

REVIEW OF THE RESULTS OBTAINED WITH AMMONIUM HALIDES.

It has already been mentioned, that the Raman spectra of ammonium halides have been investigated at different temperatures by Menzies and Mills. The

lines observed at the room temperature are all due to inner vibrations of the NH_4 group. At the temperature $-30°C.$, a new line at 160 cm.$^{-1}$ appears in the case of NH_4Cl but no such new line is observed in the case of the other two halides. The following explanation has been offered by these authors regarding this peculiar behaviour of the ammonium halides.

The crystals of NH_4Cl and NH_4Br possess body-centred cubic lattice at ordinary temperatures. The unit cell is shown diagrammatically in figure 1.
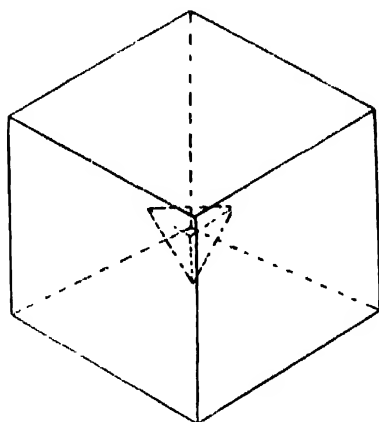
FIGURE 1.

The tetrahedron at the centre represents the ammonium ion. The chlorine ions are at the corners of the unit cell. In the case of NH_4Cl at $-30°C.$, the whole lattice is built up by mere translation along the three axes. In such an arrangement it can be easily seen that on one side of a chlorine ion along the body diagonal, a face of the tetrahedron is nearer to it while on the other side a corner of another tetrahedron is nearer to it. Hence the arrangement is asymmetric and the restoring force during lattice oscillation is also asymmetric. There is, therefore, a considerable change in the polarisability during lattice oscillation and the corresponding Raman line is intense. Above $-28°C.$, there is rotational oscillation of the NH_4 ion so that it cannot be distinguished whether there is a corner or a face of the tetrahedron opposite to the chlorine ion and therefore, the asymmetric restoring force vanishes. Hence the Raman line 160 cm^{-1} is absent at temperatures above $-28°C.$

In the case of NH_4Br the lattice is built up not by mere translations, but the tetrahedron is rotated through 90° simultaneously with primitive translation along each axis. Taking into consideration the eight cells round a *chlorine* ion, it can be easily seen that in the two cells along a body diagonal the uppermost edge of one of the tetrahedra is parallel to the lowermost edge of the other. The whole group of eight adjacent cells will possesses the symmetry elements

of a cube. With such an arrangement, on opposite sides of a *chlorine* ion, there will be either faces or corners of the two tetrahedra, and consequently the restoring force will be symmetric. For this reason, no new Raman line is observed in the case of NH_4Br crystals. It has been pointed out by Menzies and Mills that other evidences may be adduced in favour of the hypothesis regarding this arrangement of the tetrahedra in the crystals of NH_4Br. As for instance, Hettich[9] independently put forward similar hypothesis in order to explain the results of the study of piezoelectric properties of crystals of NH_4 Br and NH_4Cl. Measurement of coefficient of expansion near the transition temperature[10] as well as the results of X-ray investigation of the structure of tetramethyl ammonium bromide[11] support the above hypothesis. It has, therefore, been shown definitely by Menzies and Mills by the investigations mentioned above that the Raman line due to lattice oscillation cannot have any appreciable intensity unless the restoring force during the oscillation is asymmetric and also the asymmetric arrangement of the two cations on opposite sides of each anion is indispensably necessary for the occurrence of such an asymmetric restoring force during lattice oscillations. The case of organic crystals of known structure can also be examined from this point of view and definite conclusion can be arrived at regarding the intensity of Raman lines due to lattice oscillations in these crystals.

NATURE OF THE RESTORING FORCE DURING LATTICE OSCILLATION IN SOME ORGANIC CRYSTALS.

Naphthalene is one of the organic crystals with which strong new Raman lines have been observed close to the Rayleigh line. The structure of this crystal has been accurately determined by Banerjee.[12] The crystal belongs to the space group C_{2h}^5 in the monoclinic prismatic class. There are two molecules in the unit cell. The correct orientation of the molecules in the cell are obtained by first placing them along the $b c$ plane with the length along the c axis and then by rotating successively about the b and c axes through 25° and 12° respectively, the rotation of the two molecules being in the same direction about the b axis and in opposite directions about the c axis. The arrangement of the molecules in the unit cell is shown diagrammatically in figure 2. The centres of the two molecules may be placed at ooo and $\frac{1}{2}$o$\frac{1}{2}$. It can be seen that on the two sides of the molecules B at $\frac{1}{2}$o$\frac{1}{2}$ there are two molecules A, A which are symmetrically situated with respect to the former. Any displacement of former molecule with respect to the latter two will, therefore, produce a symmetric restoring force and consequently, the corresponding Raman line due to lattice oscillation cannot have any appreciable intensity. The Raman spectrum of solid naphthalene is reproduced in plate XIII to show that one (71 cm^{-1}) of the lines close to the Rayleigh line is nearly of the same intensity as the line
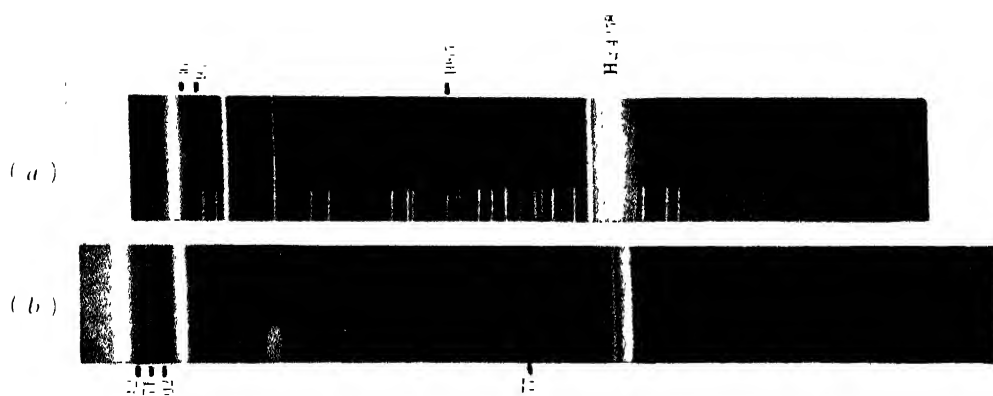
Raman Spectra of Crystals.

(a)   p — Dibromobenzene at 31°C.
(b)   Naphthalene   ,,   ,, .

1377 cm^{-1}, the latter being the most intense of all the Raman lines of naphthalene due to intramolecular vibrations (the photographic plate is almost equally sensitive in these two regions). Since the Raman line due to lattice oscillation cannot have appreciable intensity in the case of naphthalene, as has been explained above, the origin of these new lines close to the Rayleigh line cannot be attributed to lattice oscillations.
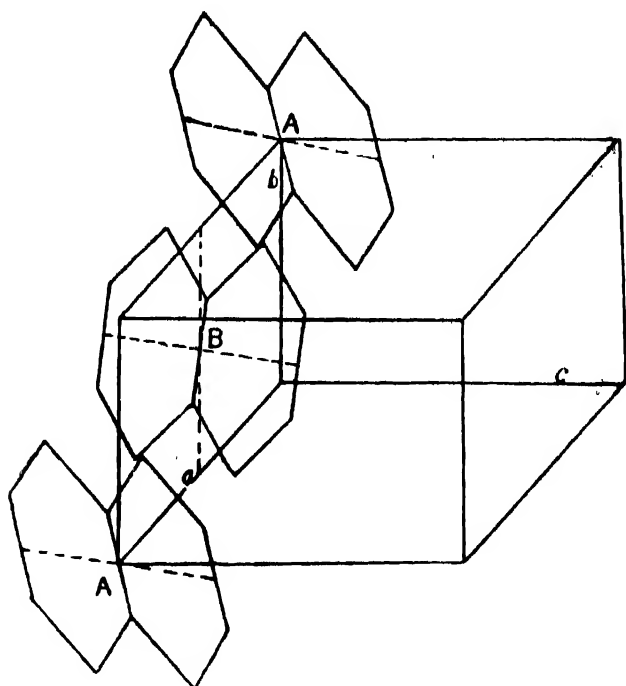
FIGURE 2.

It is evident from the arguments set forth above that the symmetric disposition of the two molecules on opposite sides of any molecule in the lattice arises out of the symmetry elements of the space group C_{2h}^5. In other crystals belonging to this space group, similar symmetric arrangement is expected. The crystals of p-dichlorobenzene and p-dibromobenzene are reported to belong to the space group C_{2h}^5 by Hendricks.[13] It has been shown by him that there is a centre of symmetry at the centre of each molecule in the unit cell, besides at a few other points in the cell. Hence in the case of these two crystals also, no asymmetric restoring force can be expected and therefore the Raman lines due to lattice oscillations cannot have appreciable intensities. Contrary to these expectations, however, actually in the case of solid p-dibromobenzene a new line at 37 cm^{-1} is observed which is about twice as intense as the most intense Raman line of the p-dibromobenzene molecule, as can be seen from plate XIII.

The integrated intensity of the band at 93 cm^{-1} is also fairly great. In the case of p-dichlorobenzene also, some of these new lines are more intense than the intense Raman lines due to intramolecular vibrations. From these results, therefore, it appears that these lines cannot have their origin in lattice oscillations.

The above considerations, therefore, lend support to the hypothesis put forward in previous papers that the new lines close to the Rayleigh line are due to intermolecular oscillations in polymerised groups.

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THE CALCULATION OF INTERPLANAR SPACINGS OF CRYSTAL SYSTEMS BY VECTORS.

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ABSTRACT. Expressions for the calculation of interplanar spacings of crystal systems : cubic, simple tetragonal, simple orthorhombic, hexagonal, simple monoclinic, triclinic and rhombohedral have been derived by vectors. This treatment is shown to be much briefer and simpler than the one given by analytical methods, which are generally employed at present for these derivations.

The method of calculating the interplanar spacings between the successive planes in any assumed crystal structure is based at present on a well-known theorem in solid analytic geometry, which gives the perpendicular distance d from any point to a plane. The derivations of the expression for d by this method, especially for lattices other than cubic, seem to be accompanied by analytical complexities. We shall derive these expressions here by vectors, which make the derivations much briefer and simpler than the analytical method.

The perpendicular distance d_{hkl} between the successive planes of a given set may be expressed as a function of the lattice constants a_o, b_o, and c_o, and of the Miller indices (hkl) of the set of planes in question as follows.

Let OX, OY and OZ be the crystal axes: a_o be the unit distance along OX, b_o along OY and c_o along OZ, and $\bar{a}$, $\bar{b}$ and $\bar{c}$ be the unit vectors along the axes respectively. Let $\bar{n}$ be the unit vector normal to plane (hkl), then,

$$\bar{n} = n_a \bar{a} + n_b \bar{b} + n_o \bar{c} \qquad \dots (1)$$

$$(\bar{n} \cdot \bar{a}) \frac{a_o}{h} = (\bar{n} \cdot \bar{b}) \frac{b_o}{k} = (\bar{n} \cdot \bar{c}) \frac{c_o}{l} = d \qquad \dots (2)$$

$$\bar{n} \cdot \bar{n} = 1 \qquad \dots (3)$$

I. *Cubic, simple tetragonal and orthorhombic lattices* :

For these lattices,

$$\alpha = \beta = \gamma = 90°$$

then,

$$\bar{a} \cdot \bar{b} = \bar{a} \cdot \bar{c} = \bar{b} \cdot \bar{c} = 0 \qquad \dots (4)$$

and

$$\bar{a} \cdot \bar{a} = \bar{b} \cdot \bar{b} = \bar{c} \cdot \bar{c} = 1. \qquad \dots (5)$$

Substituting for $\bar{n}$ in equations (2) and (3), the right hand side of equation (1), one obtains,

$$n_a(\bar{a}.\bar{a})\frac{a_o}{h} = n_b(\bar{b}.\bar{b})\frac{b_o}{k} = n_c(\bar{c}.\bar{c})\frac{c_o}{l} = d$$

or

$$n_a\frac{a_o}{h} = n_b\frac{b_o}{k} = n_c\frac{c_o}{l} = d \qquad \ldots \text{ (6)}$$

and

$$(n_a)^2 + (n_b)^2 + (n_c)^2 = 1. \qquad \ldots \text{ (7)}$$

Solving equation (6)

$$n_a = \frac{d}{a_o}\,h$$

$$n_b = \frac{d}{b_o}\,k$$

$$n_c = \frac{d}{c_o}\,l$$

Substituting the values of n_a, n_b, and n_c in equation (7) we get

$$\frac{d^2}{a_o}\,h^2 + \frac{d^2}{b_o}\,k^2 + \frac{d^2}{c_o}\,l^2 = 1.$$

Solving for d or d_{hkl}.

$$d_{hkl} = \sqrt{\frac{1}{\dfrac{h^2}{a_o^2} + \dfrac{k^2}{b_o^2} + \dfrac{l^2}{c_o^2}}} \qquad \ldots \text{ (8)}$$

(a) For a cubic lattice, $a_o = b_o = c_o$, therefore

$$d_{hkl} = \sqrt{\frac{a_o}{h^2 + k^2 + l^2}}. \qquad \ldots \text{ (9)}$$

(b) For a simple tetragonal lattice, $a_o = b_o \neq c_o$, therefore

$$d_{hkl} = \sqrt{\frac{a_o}{h^2 + k^2 + \dfrac{a_o^2}{c_o}l^2}} = \sqrt{\frac{a_o}{h^2 + k^2 + \dfrac{l^2}{c^2}}}. \qquad \ldots \text{ (10)}$$

The ratio of two units of length $c_o/a_o = c$ is called the "axial ratio."

(c)   For a simple orthorhombic lattice $a_o \neq b_o \neq c_o$, therefore

$$d_{hkl} = \sqrt{\dfrac{b_o}{\dfrac{b_o^2}{a_o} h^2 + k^2 + \dfrac{b_o^2}{c_o} l_2}} \, ,$$

or

$$d_{hkl} = \sqrt{\dfrac{b_o}{\dfrac{h^2}{a^2} + k^2 + \dfrac{l^2}{c^2}}} \qquad \qquad \dots \text{(11)}$$

where $a_o/b_o = a$, and $c_o/b_o = c$ are the axial ratios.

II.   *Hexagonal Lattice :*

then   For a hexagonal lattice, $a_o = b_o \neq c_o$, and $\alpha = \beta = 90°$, $\gamma = 120°$,

$$\bar{a} \cdot \bar{b} = -\dfrac{1}{2}, \ \bar{a} \cdot \bar{c} = \bar{b} \cdot \bar{c} = 0 \qquad \qquad \dots \text{(12)}$$

From equations (1), (2) and (3) subject to the conditions in equation (12) one obtains as before,

$$n_a \dfrac{a_o}{b} - \dfrac{1}{2} \, n_b \dfrac{a_o}{h} = d \qquad \qquad \dots \text{(13)}$$

$$-\dfrac{1}{2} \, n_a \dfrac{b_o}{k} + n_b \dfrac{b_o}{k} = d \qquad \qquad \dots \text{(14)}$$

$$n_c \dfrac{c_o}{l} = d \qquad \qquad \dots \text{(15)}$$

and $$(n_a)^2 + (n_b)^2 + (n_c)^2 - n_a n_b = 1. \qquad \qquad \dots \text{(16)}$$

Solving equations (13), (14) and (15)

$$n_a = \dfrac{2}{3} \dfrac{d}{a_o} (2h + k)$$

$$n_b = \dfrac{2}{3} \dfrac{d}{b_o} (h + 2k)$$

$$n_c = \dfrac{d}{c_o} l.$$

Substituting the values of n_a, n_b and n_c in equation (16), we get

$$d^2 \left\{ \dfrac{4}{9a_o{}^2} (2h+k)^2 + \dfrac{4}{9b_o{}^2}(h+2k)^2 + \dfrac{l^2}{c_o{}^2} - \dfrac{4}{9a_o b_o} (2h+k)\,(h+2k) \right\} = 1.$$

B

Since, for the hexagonal system $a_o = b_o \neq c_o$, therefore,

$$d^2 \left\{ \frac{4}{9a_o{}^2}(5h^2+8hk+5k^2) - \frac{4}{9a_o{}^2}(2h^2+5hk+2k^2) + \frac{l^2}{c_o{}^2} \right\} = 1$$

or

$$d^2 \left\{ \frac{4}{3a_o{}^2}(h^2+hk+k^2) + \frac{l^2}{c_o{}^2} \right\} = 1.$$

Solving for d or d_{hkl}, we get

$$d_{hkl} = \sqrt{\frac{a_o}{\frac{4}{3}(h^2+hk+k^2) + \left(\frac{a_o}{c_o}\right)l^2}}$$

or

$$d_{hkl} = \sqrt{\frac{a_o}{\frac{4}{3}(h^2+hk+k^2) + \frac{l^2}{c^2}}} \qquad \dots \ (17)$$

III.   *Simple Monoclinic Lattice*:

For a simple monoclinic lattice, $a_o \neq b_o \neq c_o$,

$$a = \gamma = 90°, \quad \text{and} \quad \beta \neq 90°, \quad \text{then}$$

$$\bar{\mathbf{a}}.\bar{\mathbf{c}} = \cos\beta, \quad \bar{\mathbf{a}}.\bar{\mathbf{b}} = \bar{\mathbf{b}}.\bar{\mathbf{c}} = 0. \qquad \dots \ (18)$$

From equations (1), (2) and (3) subject to conditions in equation (18), we get

$$n_a \frac{a_o}{h} + n_c \frac{a_o}{h} \cos\beta = d \qquad \dots \ (19)$$

$$n_b \frac{b_o}{k} = d \qquad \dots \ (20)$$

$$n_a \frac{c_o}{l} \cos\beta + n_o \frac{c_o}{l} = d \qquad \dots \ (21)$$

and

$$(n_a)^2 + (n_b)^2 + (n_c)^2 + 2n_a n_c \cos\beta = 1 \qquad \dots \ (22)$$

Solving equations (19), (20) and (21),

$$n_a = \frac{d}{\sin^2\beta}\left(\frac{h}{a_o} - \frac{l}{c_o}\cos\beta\right)$$

$$n_b = \frac{d}{b_o}k$$

$$n_c = \frac{c}{\sin^2\beta}\left(\frac{l}{c_o} \quad \frac{h}{a_o}\cos\beta\right).$$

Substituting the values of n_a, n_b and n_c in the equation (22), we get

$$d^2 \left[\frac{1}{\sin^2 \beta} \left\{ \left(\frac{h}{a_o} \right)^2 + \left(\frac{l}{c_o} \right)^2 - \frac{2hl}{a_o c_o} \cos \beta \right\} + \left(\frac{k}{b_o} \right)^2 \right] = 1.$$

Solving for d or d_{hkl},

$$d_{hkl} = \sqrt{\frac{b_o}{\dfrac{\left(\dfrac{h}{a} \right)^2 + \left(\dfrac{l}{c} \right)^2 - \dfrac{2hl}{ac} \cos \beta}{\sin^2 \beta} + k^2}} \qquad \dots (23)$$

IV. *Triclinic Lattice*:

For the triclinic lattice, $a_o \neq b_o \neq c_o$, and $\alpha \neq \beta \neq \gamma \neq 90°$, then

$$\bar{a} \cdot \bar{b} = \cos \gamma, \quad \bar{a} \cdot \bar{c} = \cos \beta, \text{ and } \quad \bar{b} \cdot \bar{c} = \cos \alpha \qquad \dots (24)$$

From equations (1) and (2) we obtain

$$n_a \frac{a_o}{h} + n_b (\bar{a} \cdot \bar{b}) \frac{a_o}{h} + n_c (\bar{a} \cdot \bar{c}) \frac{a_o}{h} = d \qquad \dots (25)$$

$$n_a (\bar{a} \cdot \bar{b}) \frac{b_o}{k} + n_b \cdot \frac{b_o}{k} + n_c (\bar{b} \cdot \bar{c}) \frac{b_o}{k} = d \qquad \dots (26)$$

and $\qquad n_a (\bar{a} \cdot \bar{c}) \dfrac{b_o}{k} + n_b (\bar{b} \cdot \bar{c}) \dfrac{c_o}{l} + n_c \dfrac{c_o}{l} = d \qquad \dots (27)$

Substituting the values of $\bar{a} \cdot \bar{b}$, $\bar{a} \cdot \bar{c}$, and $\bar{b} \cdot \bar{c}$ from equation (24) in equations (25), (26) and (27), and simplifying, we get

$$\qquad \dots (28)$$

$$n_a + n_b \cos \gamma + n_c \cos \beta = \frac{d}{a_o} h$$

$$n_a \cos \gamma + n_b + n_c \cos \alpha = \frac{d}{b_o} k \qquad \dots (29)$$

$$n_a \cos \beta + n_b \cos \alpha + n_c = \frac{d}{c_o} l \qquad \dots (30)$$

Solving equations (28), (29) and (30) for n_a, n_b and n_c by the method of determinants, we get

$$
n_a = \frac{\begin{vmatrix} d\dfrac{h}{a_o} & \cos\gamma & \cos\beta \\[2mm] d\dfrac{k}{b_o} & 1 & \cos\alpha \\[2mm] d\dfrac{l}{c_o} & \cos\alpha & 1 \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}}
$$

$$
n_b = \frac{\begin{vmatrix} 1 & d\dfrac{h}{a_o} & \cos\beta \\[2mm] \cos\gamma & d\dfrac{k}{b_o} & \cos\alpha \\[2mm] \cos\beta & d\dfrac{l}{c_o} & 1 \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}}
$$

$$
n_c = \frac{\begin{vmatrix} 1 & \cos\gamma & d\dfrac{h}{a_o} \\[2mm] \cos\gamma & 1 & d\dfrac{k}{b_o} \\[2mm] \cos\beta & \cos\alpha & d\dfrac{l}{c_o} \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}}
$$

From equation (3) it follows :

$$\bar{n}.(n_a\bar{a}+n_b\bar{b}+n_c\bar{c})=1$$

or
$$(\bar{n}.\bar{a})n_a + (\bar{n}.\bar{b})n_b + (\bar{n}.\bar{c})n_c = 1. \qquad \ldots (31)$$

From equation (2) one obtains

$$\bar{n}.\bar{a} = d\,\frac{h}{a_o}, \quad \bar{n}.\bar{b} = d\,\frac{k}{b_o}, \text{ and } \bar{n}.\bar{c} = d\,\frac{l}{c_o}.$$

Substituting the values of $\bar{n}.\bar{a}$, $\bar{n}.\bar{b}$, $\bar{n}.\bar{c}$, n_a, n_b and n_c as obtained above, in equation (31), we get

$$\frac{d\frac{h}{a_0}\begin{vmatrix} d\frac{h}{a_o} & \cos\gamma & \cos\beta \\ d\frac{k}{b_o} & 1 & \cos\alpha \\ d\frac{l}{c_o} & \cos\alpha & 1 \end{vmatrix} + d\frac{k}{b_o}\begin{vmatrix} 1 & d\frac{h}{a_o} & \cos\beta \\ \cos\gamma & d\frac{k}{b_o} & \cos\alpha \\ \cos\beta & d\frac{l}{c_o} & 1 \end{vmatrix} + \frac{dl}{c_o}\begin{vmatrix} 1 & \cos\gamma & d\frac{h}{a_o} \\ \cos\gamma & 1 & d\frac{k}{b_o} \\ \cos\beta & \cos\alpha & d\frac{l}{c_o} \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}} = 1 \qquad \ldots (32)$$

This may be simplified to

$$\frac{\left\{\frac{d}{b_o}\right\}^2\frac{h}{a}\begin{vmatrix} \frac{h}{a} & \cos\gamma & \cos\beta \\ k & 1 & \cos\alpha \\ \frac{l}{c} & \cos\alpha & 1 \end{vmatrix} + \left\{\frac{d}{b_o}\right\}^2 k\begin{vmatrix} 1 & \frac{h}{a} & \cos\beta \\ \cos\gamma & k & \cos \\ \cos\beta & \frac{l}{c} & 1 \end{vmatrix} + \left\{\frac{d}{b_o}\right\}^2\frac{l}{c}\begin{vmatrix} 1 & \cos\gamma & \frac{h}{a} \\ \cos\gamma & 1 & k \\ \cos\beta & \cos\alpha & \frac{l}{c} \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}} = 1$$

Solving for d or d_{hkl}.

$$d_{hkl} = \sqrt{\dfrac{\begin{vmatrix} \frac{h}{a} & \cos\gamma & \cos\beta \\ k & 1 & \cos\alpha \\ \frac{l}{c} & \cos\alpha & 1 \end{vmatrix} \frac{h}{a} + k \begin{vmatrix} 1 & \frac{h}{a} & \cos\beta \\ \cos\gamma & k & \cos\alpha \\ \cos\beta & \frac{l}{c} & 1 \end{vmatrix} + \frac{l}{c} \begin{vmatrix} 1 & \cos\gamma & \frac{h}{a} \\ \cos\gamma & 1 & k \\ \cos\beta & \cos\alpha & \frac{l}{c} \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}}} \qquad \dots (33)$$

(d) For the rhombohedral lattice, $a_o = b_o = c_o$, and $\alpha = \beta = \gamma \neq 90°$. Then,

$$\bar{a} \cdot \bar{b} = \bar{a} \cdot \bar{c} = \bar{b} \cdot \bar{c} = \cos\alpha. \qquad \dots (34)$$

When these values are substituted in question (32), it becomes

$$\dfrac{\left(\frac{d}{a_o}\right)^2 h \begin{vmatrix} h & \cos\alpha & \cos\alpha \\ k & 1 & \cos\alpha \\ l & \cos\alpha & 1 \end{vmatrix} + \left(\frac{d}{a_o}\right)^2 k \begin{vmatrix} 1 & h & \cos\alpha \\ \cos\alpha & k & \cos\alpha \\ \cos\alpha & l & 1 \end{vmatrix} + \left(\frac{d}{a_o}\right)^2 l \begin{vmatrix} 1 & \cos\alpha & h \\ \cos\alpha & \cos\alpha & k \\ \cos\alpha & 1 & l \end{vmatrix}}{\begin{vmatrix} 1 & \cos\alpha & \cos\alpha \\ \cos\alpha & 1 & \cos\alpha \\ \cos\alpha & \cos\alpha & 1 \end{vmatrix}} = 1$$

Solving for d or d_{hkl}.

$$d_{hkl} = \sqrt{\dfrac{h \begin{vmatrix} h & \cos\alpha & \cos\alpha \\ k & l & \cos\alpha \\ l & \cos\alpha & 1 \end{vmatrix} + k \begin{vmatrix} \cos\alpha & h & \cos\alpha \\ l & k & \cos\alpha \\ \cos\alpha & e & 1 \end{vmatrix} + \begin{vmatrix} \cos\alpha & \cos\alpha & h \\ l & \cos\alpha & k \\ \cos\alpha & l & l \end{vmatrix}}{\begin{vmatrix} 1 & \cos\alpha & \cos\alpha \\ \cos\alpha & l & \cos\alpha \\ \cos\alpha & \cos\alpha & l \end{vmatrix}}}$$

$$= \frac{a_0 \sqrt{1 + 2\cos^3\alpha - 3\cos^2\alpha}}{\sqrt{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + hl + kl)(\cos^2\alpha - \cos\alpha)}} \quad \cdots \; 35$$

SUMMARY

Formulas for the calculation of interplanar spacings of crystal systems are derived by a vector method, which is much briefer and simpler to use than the analytical method. The results are summarized in table I :

TABLE I.

Lattice.	Characteristic.	No. of equation giving value for d_{hkl}.
I. Rectangular	$\alpha = \beta = \gamma = 90°$	
a. Cubic	$a_0 = b_0 = c_0$	(9)
b. Simple tetragonal	$a_0 = b_0 \neq c_0$	(10)
c. Simple orthorhombic	$a_0 \neq b_0 \neq c_0$	(11)
II. Hexagonal	$a_0 = b_0 \neq c_0$	
	$\alpha = \beta = 90°, \gamma = 120°$	(17)
III. Simple monoclinic	$a_0 \neq b_0 \neq c_0$	
	$\alpha = \gamma = 90°, \beta \neq 90°$	(23)
IV. Triclinic	$a_0 \neq b_0 \neq c_0$	
	$\alpha \neq \beta \neq \gamma \neq 90°$	(33)
V. Rhombohedral	$a_0 = b_0 = c_0$	
	$\alpha = \beta = \gamma \neq 90°$	(35)

DEPARTMENT OF PHYSICS,
UNIVERSITY OF PITTSBURGH,
PITTSBURGH, PENNSYLVANIA,
U. S. A.

Obituary Notices

SIR J. C. BOSE

By the death of Sir Jagadish Chandra Bose, F.R.S., D.Sc., LL.D., at Giridih on Tuesday, the 23rd of November, 1937 at the age of 79, the scientific world has lost a research worker and an original investigator of a very high order. After graduating at St. Xavier's College, Calcutta, he went over to England for higher studies, and joined the University College, London, where he studied Botany as his special subject. He also studied Physics under Lord Rayleigh at Cambridge. He came back to India in 1884 and was appointed as Professor of Physics, Presidency College, Calcutta from which he retired in 1915 as Emeritus Professor. Many universities in Great Britain and India recognised his scientific abilities and paid him academic honours. He was awarded the C.I.E. and C.S I. and in 1917 received Knighthood.

He was a delegate to the International Scientific Congress held in 1900 and also the scientific member of deputation to Europe and America in 1907, 1914 and 1919.

He published numerous papers among which a few can be mentioned below :—

(1) Index of Refraction of Glass for the Electric Ray. (Proc. Roy. Soc., 1897.)

(2) On the Influence of Thickness of Air Space on Total Refraction of Electric Radiation. (Proc. Roy. Soc., 1897.)

(3) On the Selective Conductivity Exhibited by certain Polarising Substances. (Proc. Roy. Soc , 1897.)

(4) The Production of a Dark Cross in the Field of Electromagnetic Radiation. (Proc. Roy. Soc., 1898.)

(5) On the Electric Touch and the Molecular Change produced in Matter by Electric Waves. (Proc. Roy. Soc., 1900.)

(6) On the Similarity between Radiation and Mechanical Strain. (Proc. Roy. Soc., 1901.)

(7) On the Strain Theory of Photographic Action. (Proc. Roy. Soc., 1901.)

(8) On the Change of Conductivity of Metallic Particles under Cyclic Electromotive Variation. (Brit. Assoc. Glasgow, 1901.)

(9) Electromotive Wave accompanying Mechanical Disturbance in Metals in Contact with Electrolyte. (Proc. Roy. Soc., 1902.)

(10) On the Continuity of Effect of Light and Electric Radiation on Matter.

Besides, he was the author of a large number of papers on Plant Physiology. A connected account of his investigation in this domain is to be found in his books, Response in the Living and the Non-living published as early as 1902, as well as in Plant Response, Electro-Physiology of Plants, Irritability of Plants ; Life Movements in Plants, Vols. I and II ; Life Movements in Plants, Vols. III and IV ; the Ascent of Sap, the Physiology of Photo-Synthesis ; Nervous Mechanism of Plants ; Motor Mechanism of Plants ; Plant Autographs and their Revelations ; Tropic Movement and Growth of Plants.

After his retirement from the Government service he founded the Bose Research Institute in 1917 and was the Founder Director all the time.

PROF. LALJI SRIVASTAVA.

We extremely regret to record the death of Prof. Lalji Srivastava. He was a member of the Indian Association for the Cultivation of Science and a Professor of the Ajmere College, Rajputana.

A METHOD OF MEASURING MINUTE RADIO-FREQUENCY ALTERNATING CURRENT AND ITS APPLICATION TO THE ABSOLUTE MEASUREMENT OF FIELD-STRENGTHS OF WEAK RADIO SIGNALS.*

BY ALI IMAM, M.Sc., SUKHAMAYA GANGOPADHYAYA, M.Sc.,

AND

S. R. KHASTGIR, D.Sc.,

Dacca University.

ABSTRACT. Martyn's method has been adopted in a modified form to measure radio-frequency alternating currents of the order of 10^{-6} ampere. The method has been applied to the absolute determinations of the field-strengths of weak signals. The details of the method and of its application are given in the paper.

The day value at Dacca of the field-strength of the V. U. C. station (Calcutta) has been determined. From a knowledge of the metre-amperage of the station, the Austin-Cohen coefficient has been calculated.

The field-strengths of the night signals from the same station and also from the V. U. D. (Delhi) station have also been determined.

A. *Measurement of minute radio-frequency alternating current.*

INTRODUCTION.

The thermionic valve has been used directly as a means of current measurement in a manner comparable to that employed in the measurement of voltages by the Moullin thermionic voltmeter. If we pass the current to be measured through the filament of a diode valve and note the plate current which is caused to flow, it is possible to deduce the value of the heating current in the filament ·from the characteristics of the valve. But in this case it is evident that readings can only be obtained with comparatively large currents which can be more conveniently measured by other methods. It was J. H. Turnbull[1] who adopted this method by simply superposing the small alternating current to be measured on to a steady direct heating current supplied by an accumulator. Turnbull's method is not however suitable for the measurement of very small alternating currents.

* Communicated by the Indian Physical Society.

D. F. Martyn [2] modified the method and made it very sensitive by using alternating current for the supply of the main heating current of the filament. If the frequency of the current be exactly the same as the frequency of the current to be measured, then the effects of the main current and the superimposed small current is additive when they are in the same phase and it is then possible to evaluate the current to be measured from the valve characteristic.

A similar but a simpler procedure has been adopted in this investigation for the measurement of small alternating currents. We shall describe now the details of our experimental procedure.

EXPERIMENTAL PROCEDURE.

(a) *Arrangements for measuring an extremely small alternating current.*
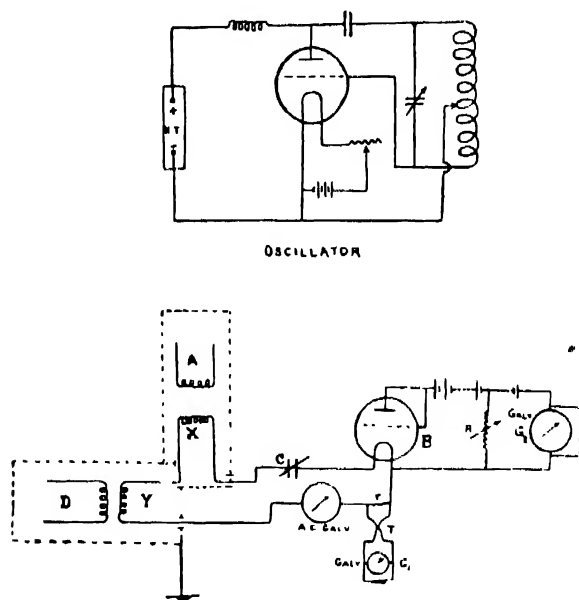
FIGURE I.

The arrangement of the apparatus is shown in figure 1. A is a screened Hartley oscillator capable of supplying enough current to feed the filament current of the valve in the circuit B through mutual induction. The filament of the valve has been joined in series with two suitable coils X and Y, a suitable variable condenser C, and an A.C. milli-ammeter (reading only up to a minimum of 5 m.a.). The circuit has also a suitable small resistance r in series, and a vacuum thermal junction T has been connected across this small resistance. The inductance coil in the Hartley circuit has been loosely coupled to the coil X and the induced current in its circuit is indicated by the A. C. milli-ammeter and

also by a sensitive mirror galvanometer G_1 connected to the vacuum junction. The resistance r has been chosen in such a way that only a very small fraction of the current well within the maximum allowable current passes through the heating coil of the vacuum junction. This circuit is then accurately tuned to the frequency of the oscillator A by noting the maximum deflection in the galvanometer G_1. The valve used in the circuit B is a screen-grid valve. A suitable voltage has been given to the plate and the screen-grid which have been connected together. Since our object has been to measure a change of the order of microamperes in the plate current which amounts to several milliamperes, a balancing device has been employed.

(b)   *The balanced galvanometer G_2.*

A variable resistance R of several hundred ohms has been placed in series with the plate battery. Shunted across this high resistance has been placed a two-volt accumulator in series with a mirror galvanometer G_2. The value of this variable resistance R is adjusted to give zero reading on the galvanometer G_2. If r_g be the resistance of this galvanometer, then a change of plate current of amount i_p results in a change of current through the galvanometer of amount

$$i_g = \frac{R}{R + r_g}$$

. Since R is large compared with r_g, $i_g = i_p$, *i.e.*, the full change of plate current is measured by the galvanometer G_2. A very minute alternating current can be induced through the coil Y which is loosely coupled to the inductance coil of another Hartley oscillator D. The oscillator D and the coil Y have been enclosed in a well-shielded wooden box. The oscillator D is adjusted to have exactly the same frequency as that of the oscillator A. By adjusting the distance of the coil Y from the oscillator D an extremely small current produced by mutual induction is superposed on to the large current flowing through the same circuit giving no indication in the A. C. milli-ammeter, but producing a small deflection in the galvanometer G_1 connected to the vacuum junction. The galvanometer G_2 which has previously been set to zero or thereabout by adjusting the variable resistance R then produces a large deflection. The change in this deflection which is due to the superposition of a minute alternating current to the tuned circuit is then noted.

(c)   *Calibration of the galvanometer G_2.*

The original current through this tuned circuit has been such that for the valve in the circuit B *a change in the filament current produces a proportionate change in the plate current.* With the particular valve the characteristic curve showing plate current against the filament current for a fixed plate voltage (100 V) has been drawn and it is found that over a range

the curve is a straight line. By varying the tilt of the coil X which is near the inductance loop of the oscillator A, the current through the filament is adjusted to have a definite value within this range (62·9 m.a. corresponding to 30 scale divisions of the milli-ammeter). The position of the spot of light corresponding to the deflected position of the galvanometer connected to the thermo-junction is then noted. The G_2-galvanometer circuit is however kept disconnected. On increasing the filament current to 68·0 m.a. (corresponding to 35 scale divisions of the milli-ammeter) the spot of light corresponding to the deflection of the galvanometer G_1 is again noted. Thus corresponding to an increase of current 5·1 m.a. the change in the deflection of the galvanometer connected to the thermo-junction is determined. Next after connecting the galvanometer G_2 and making the balancing arrangements, the filament current is increased from 62·9 m.a. by a suitable amount as indicated by the change in the deflection of the galvanometer connected to the thermo-junction so as to give an almost full-scale deflection in the balanced galvanometer G_2. Since the alternating current in milliamperes through the thermo-junction has been found for this range to be proportional to the deflection in the galvanometer connected to the thermo-junction, the current for the full-scale deflection in the balanced galvanometer can then be estimated. The galvanometer G_2 is thus calibrated.

This will be made clear from an actual set of readings :

A change from 30 to 35 scale divisions in the milli-ammeter produced a change in the deflection of the galvanometer G_1 connected to the thermo-junction equal to 50 scale divisions.

Thus 50 scale divisions of the galvanometer $G_1 \equiv 5·1$ m.a.

Again it was found that corresponding to a change of 6·5 scale divisions of the galvanometer G_1 the change in the deflection of the galvanometer G_2 amounted to 400 divisions.

Therefore 1 scale division of the galvanometer G_2.

$$\frac{5·1 \times 6·5}{50 \times 400} \times 10^{-3} \text{ amp.} = 1·66 \times 10^{-6} \text{ amp.}$$

Now when a small alternating current is induced into the circuit by switching on the oscillator D, the observed change in the deflection of the galvanometer G_2 which would be proportional to the amplitude of the current can then be evaluated.

It has thus been possible to accurately measure by this method radio-frequency alternating currents of the order of 10^{-6} amperes.

B. *Absolute measurements of field-strengths of weak radio-signals.*

INTRODUCTION.

We have applied this method of measuring minute alternating current to the absolute measurements of field-strengths of weak radio signals. Having measured small alternating currents passing through a small known impedance it has been possible to impress extremely small known voltages across the input terminals of a receiving set. The receiving set is thus calibrated and the field-strengths during the day and the night of the V. U. C. (Calcutta) station of the Indian State Broadcasting Service estimated. The night-field-strengths of the V. U. D. (Delhi) station have also been determined.

METHOD OF RECORDING CHANGES IN THE GALVANO-METER DEFLECTION DUE TO THE SIGNALS.
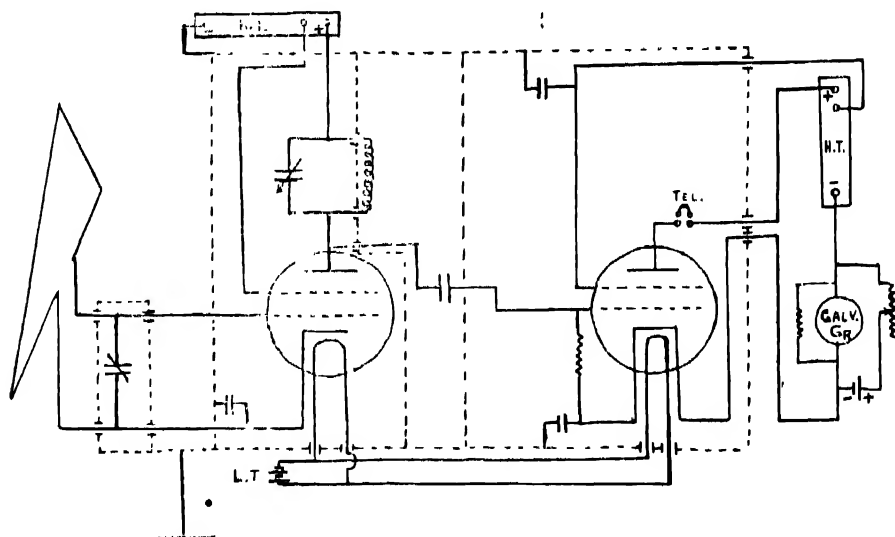
FIGURE 2.

A two-valve receiving set has been employed—the diagram of which is given in figure 2. A Mazda (A.C.S.G) valve has been used for the H. F. amplification. The filament has been indirectly heated by D. C. from a storage battery. The tuned anode circuit of the H. F. valve has been followed by a leaky grid detector (A. C. S$_2$ valve fed by D. C.). A potentiometer circuit has been built up to balance the no-signal anode current of the detector valve. A separate H. T. battery has been employed for the detector stage. A mirror galvanometer G$_R$ has been used in the balancing arrangement. Lamp and scale arrangements have been used for taking galvanometer readings

A triangular frame aerial with a shielded tuning condenser across it has been used with the receiving set. The aerial has been permanently fixed in a vertical plane pointing towards the direction of the V. U. C. station.

With the aerial on, the receiver is tuned to the modulated waves from the V. U. C. station with the help of the pair of telephones. The galvanometer is then connected and the plate current of the detecting valve is balanced with the aerial off. The changes in the galvanometer deflection are then recorded with the aerial switched on. The zero reading of the scale has been checked every time for each observation. The checking has been very conveniently done by short-circuiting the tuning condenser in the receiving set. In fact it has been found very convenient to keep the aerial connected to the input terminals of the receiver and to take readings with the switch short-circuiting the tuning condensor on and off.

CALIBRATION OF THE RECEIVING SET.
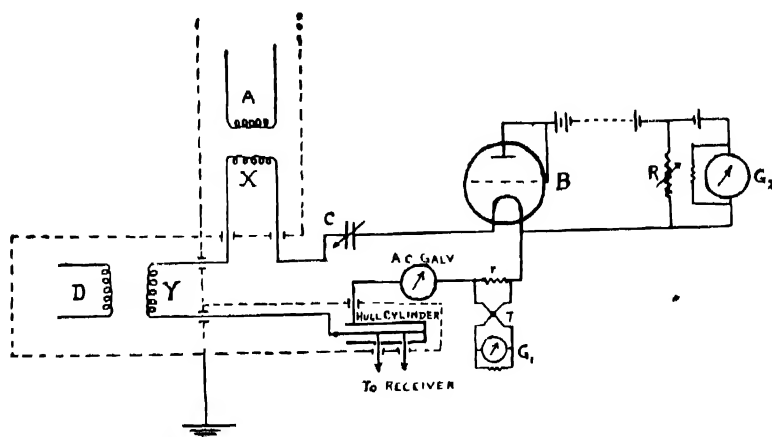
FIGURE 3.

Previous to the recording of the changes in the galvanometer deflections due to radio signals or subsequently the receiving set has been calibrated. Small known voltages have been applied to the input terminals of the receiver and the corresponding changes in the galvanometer deflection noted.

For the calibration work a Hull cylinder has been placed in series with the filament of the valve in the circuit B, a suitable variable condenser C the coils X and Y, the A. C. milli-ammeter and a small resistance r across the terminals of which is inserted a vaccum junction (See fig. 3.). It consists of a copper rod ('56 cm. in diameter) surrounded by a concentric brass cylinder (internal diameter 3.11 cm.). One end of the cylinder is open while the other end is closed by a brass disc sweating into the cylinder. The copper rod is also uxed at that end. Two copper wires have been soldered to the middle of

the copper rod at a distance of 9 cm. from each other and led out through small holes in the outer cylinder. The Hull-cylinder has been enclosed inside a metal box which is put to earth. When a small alternating current is induced into the tuned Hull cylinder circuit by switching on the oscillator D, the potential drop between the two points on the rod from which the two wires are led out is equal to (L. w. i 1) where w is the angular frequency of the alternating current i, L is the inductance per cm. and 1 the distance between the tapping points. The value of L is given by

$$L = \log_e \frac{R}{r} \quad (c.\ m.\ u.)\ \text{per cm.}$$

$$= \cdot 0046 \log_{10} \frac{R}{r}\ \text{per cm.}$$

where r and R are the outer radius of the rod and the inner radius of the cylinder respectively. This inductive potential drop producing a certain change in the deflection of the receiving set galvanometer can be calculated if the current is known.

We have already described how this small current is to be measured. The value of this current i as estimated from the change in the deflection of the previously calibrated galvanometer G_2, requires however a correction. In the experiment where the additional small current flowing through the circuit (including the filament) is estimated from the change in the deflection of the galvanometer G_2, a large current (about 63 m.a.) flows through the circuit, whereas in the experiment where the change in the deflection of the receiving set galvanometer (G_n) due to a small potential difference developed between the tapping points on the Hull cylinder is noted, only a very minute alternating current passes through the same circuit. The H. F. resistance of the filament in the former case is much greater than that in the latter.

If R_0 is the H. F. resistance of the entire circuit when a large current of 62·9 m. a. is passing through it and R the corresponding value when an extremely small current flows through the circuit, the correct value of the small current will be R_0/R times the " apparent " value of the current as estimated from the change in the deflection of the galvanometer G_2. Now R_0 can be easily determined. For the measurement of R, a calibration curve has been first drawn showing the changes in the deflection of the balanced galvanometer G_n in the receiver due to different (uncorrected) voltages produced by passing known values of the uncorrected current through the circuit containing the Hull cylinder when the tapping points from the latter are connected to the input terminals of the receiver. Next a change in the deflection of the galvanometer G_n *exactly equal to* that due to the signal voltage is produced by passing a suitable small

current through the same tuned circuit. The circuit is then distuned by varying the condenser and a curve obtained giving the changes in the deflection of the galvanometer G_k for the different capacity-values of the condenser. Making use of the previously drawn calibration curve a resonance curve is drawn showing the uncorrected current in the Hull cylinder circuit producing voltages which are applied to the input terminals of the receiving set for the different values of the condenser. As explained below the H. F. resistance of the circuit is determined from this uncorrected rosonance curve.

In constructing the resonance curve when the circuit is distuned, different values of the current have actually passed through the circuit containing the filament and therefore the values of the H. F. resistance of the circuit are not the same for all the currents. *We can however assume without any serious error that the H. F. resistance is practically the same for the resonance current i and the distuned current i'* which has been usually ·707i. The correct values of these currents within this limited range (i to ·707i) can therefore be taken proportional to their apparent values which have already been estimated with the help of the calibrated galvanometer G_2. Thus the ratio of the resonance current to the distuned current remains the same whether the values of the currents are corrected or not. Thus having obtained the value of R of the circuit carrying a current which causes the same deflection in the receiving set as the signal voltage and also the value of R_0 of the same circuit carrying the large current, the correct signal voltage can be estimated.

The field-strength is then obtained from

$$E = \frac{V. 7\cdot6. R}{A. N. f^2. L} . 10^{10} \text{ volts/metre, where}$$

N = no. of turns of wire in the loop aerial

A = area of the loop in sq. cm.

R = total radio-frequency loss-resistance of the loop in ohms.

L = Inductance of the loop in henrys.

and f = frequency of the waves in cycles per second.

In our experiments $L = 32\cdot6\mu H$

$R = 55\cdot75$ ohms.

$N = 2$

$A = 5\cdot604 \times 10^4$ sq. cm.

and $f = \cdot809 \times 10^6$ cycles/sec.

so that $E = 1\cdot77 \times V$ volts/metre.

MEASUREMENTS OF THE FIELD-STRENGTH OF THE DAY-SIGNAL FROM THE V.U.C. STATION OF THE INDIAN STATE BROADCASTING CO.

Continuous observations of the galvanometer deflection have been taken every $\frac{1}{2}$ min. during the day when the Calcutta signal is on. All motors and generators, etc., in the laboratory have been stopped during the time of the observations. We give below the successive values of the changes in the galvanometer deflections recorded on 28-3-37.

Dacca time :   Changes of galvanometer deflections.

10 A.M.   12, 9, 10, x, 10, 13, 13, 16, 12, 15, 10. 13, 13, 14, 10, 13, 11.
               13. 17, 8, 15, 5, 12, 13, 14, 12, 10, 12˙5 9˙5, 9, 15˙5 scale
               divisions.
                         Mean : 12˙27 scale divisions.

10-32 A.M.   … 11, 15, 11, 15, 10, 9, 12, 15˙5, 10˙5, 9˙5, 11, 12, 12, 16, 9,
               14˙5, 13, 10, 11, 11, 14, 15, 10˙5, 10, 14, 11˙5, 14, 12˙5, 12,
               10˙5, 13˙5, scale divisions.
                         Mean : 12˙15 scale divisions.

11-20 A.M.   … 9, 10, 10, 14, 11, 15, 8, 14, x, 15, 16, 11, 12, 10˙ 5, 10, 12˙5,
               16, 12, 17, 17˙5, 14, 10, 13, 10, x, 12, 11, 10, 14˙5, 16˙5,
               scale divisions.
                         Mean ; 12˙51 scale divisions.

11-40 A.M.   … 11˙5, 10˙5, 13, 11, 14˙5, 12, 14, 15˙5, 17, 12˙5, 17. 9, 10, 14,
               14˙5, 17, 9, 14, 10, 16, ˙14, 10, 16, 11, 18, 16, 15, 16,
               scale divisions.
                         Mean : 13˙57 scale divisions.

11-55 A.M.   … 17˙5, 13, 13˙5, 14, 18, 20, 14, 20, 20, 20, 17, 20˙5, 17, 13˙5,
               12, 17, 18˙5, 15. 19˙5, 14, 17, 14, 18, 9, 16, 13,
               14, 15, 16, scale divisions.
                         Mean : 15˙93 scale divisions.

The average of these mean values = 13˙28 scale divisions.

The calibration curve showing the changes in the deflection of the receiving set galvanometer for different uncorrected applied voltages is shown in figure 4. The data for the calibration curve are given in table I.

The applied uncorrected voltage is given by (L.w.l) × i

In our experiments L = Inductance per cm. between the tapping points on the Hull cylinder

$$= ˙0031 \ \mu H$$

$$l = 9 \ cm.$$

$$w = 2\pi f = 2\pi \times ˙809 \times 10^6 = ˙509 \times 10^7$$

∴ Hence the applied uncorrected voltage $= i \times 14˙19 \times 10^{-2} = i \times Z$, where

$$Z = 14˙19 \times 10^-$$

2
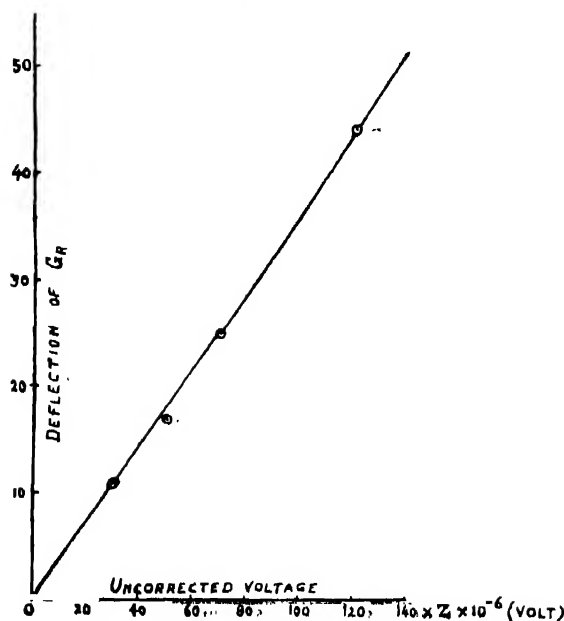
FIGURE 4.

It can be seen from the calibration curve in figure 4 that a deflection of $13\cdot28$ divs. in the galvanometer G_R is due to an uncorrected voltage of $(3\cdot6 \times 10^{-8} \times Z)$ volts.

The correct signal voltage is obtained by multiplying this by $\dfrac{R_0}{R}$.

TABLE I

1 div. of the galvanometer $G_2 = 10\cdot17 \times 10^{-6}$ amp.

Deflection of G_2	Uncorrected voltage $i \times Z \times 10^{-6}$ volt	Deflection of G_R
3	$30\cdot5 \times Z \times 10^{-6}$	11
5	$50\cdot84$,,	17
7	$71\cdot2$,,	25
12	$122\cdot02$,,	44

The H. F. resistance of the entire circuit carrying $62\cdot9$ m.a. of current $= R_0 = 95\cdot34$ ohms.

The H. F. resistance R of the same circuit carrying a current in the circuit and producing the same galvanometer deflection in G_R as that due to the signal voltage has been determined. The data for the resonance curve from which R is determined are given in table II and figure 5.
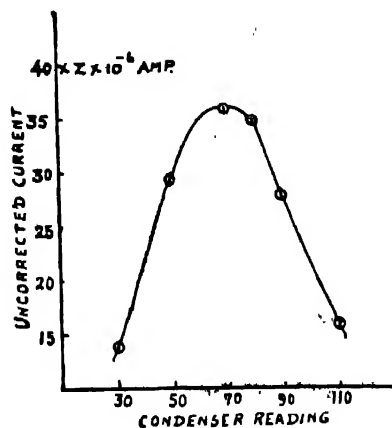
FIGURE 5.

TABLE II

Condenser reading.	deflection of G_R .	Uncorrected current $\times Z \times 10^{-6}$ (from calibration curve).
30	5	$14 \times Z \times 10^{-6}$
50	9	25 ,,
70	13	36 ,,
80	11	30 ,,
90	10	28 ,,
110	6	16 ,,

Here

$$C_a \equiv 95 \text{ divs.} = \cdot 0004095 \, \mu F$$

$$C_b \equiv 47 \text{ divs.} = \cdot 000316 \, \mu F$$

$$C_r = \cdot 0003975 \, \mu F, \quad m = 1$$

$$L = \text{Inductance of the circuit} = 113 \cdot 7 \, \mu H$$

$$\lambda = 370 \cdot 4 \text{ metres.}$$

Then $R = \dfrac{L . \pi . 3 \times 10^{10}}{\lambda} \left(\dfrac{C_a - C_b}{C_r^2} \right) = 17 \cdot 08 \text{ ohms.}$

Hence the signal voltage $= \dfrac{95 \cdot 54}{17 \cdot 08} \times 3 \cdot 6 \times 10^{-5} \times Z$

$$= 20 \cdot 14 \times 10^{-5} \times Z \text{ volts.}$$

The average value of the day field-strength on 28-3-37 is $1.77 \times 20.14 \times 10^{-5} \times 14.19 \times 10^{-2} = 50.6\ \mu V/\text{metre}$.

The values of the day field-strength on two other days are entered below :

Day.	Time.	Field strength.
14·3·37	11·54 a.m.	49·0 $\mu V/m$
21·3·37	11·50 a.m.	57·7 $\mu V/m$

N.B. The antenna effect has not been considered in these measurements. The aerial has been inside a room under iron beams. The measurements of field-strengths are subject to these limitations.

CALCULATION OF THE AUSTIN-COHEN COEFFICIENT :

The Austin-Cohen formula is

$$E = \frac{377\ h\ I}{r\ \lambda} \cdot \frac{-\frac{a\eta}{e\sqrt{\lambda}}}{} \quad \text{micro-volts/meter.}$$

(lengths are measured in km. and current in amperes.)

For the V. U. C. station, the wavelength $\lambda = 370.4$ m., the effective height of the aerial $h = 23$ metres and the aerial current $I = 19$ amperes and $r =$ distance between Dacca and Calcutta = 240 km.

Taking the day value of the field-strength E to be $49\ \mu V/\text{meter}$, the Austin-Cohen coefficient $a = .0092$

If we take $E = 57.7\ \mu V/m$, $a = .0088$.

FIELD-STRENGTHS OF THE NIGHT-SIGNALS.

The values of night signals are on the average considerably higher than those of the day-signals. The difficulty in the correct evaluation of the field-strength of the night signal is the constant fading at night. Continuous observations for about 15 min. have been taken every half minute, of the changes of the galvanometer deflection at different times of the early part of night (from 7 to 10-30 P. M.). The mean value of each set of observations has been found to be different at different times. Previous to recording the changes in the galvanometer deflections or subsequently a curve has been constructed showing changes in the galvanometer deflections G_R for different apparent values of the voltages applied to the input of the receiver. The range of the curve has been made to cover all the changes of galvanometer deflections due to varying signal intensities.

The apparent value of the voltage corresponding to a change in the galvanometer deflection equal to the average of a set of observed changes of deflection due to the signal is then found from the calibration curve. The correct value of the signal voltage has been determined as follows : The values of the H. F. resistance of the Hull cylinder circuit are measured for the different uncorrected currents which develop voltage differences within the appropriate range between the tapping points on the Hull cylinder. A curve is next drawn showing the values of the H. F. resistance of the circuit for the different values of the uncorrected current. From this curve the H. F. resistance R of the circuit corresponding to each current producing galvanometer deflection equal to the average of each set of observed changes of deflection due to the signal has been obtained. Thus knowing the H. F. resistance R_0 of the circuit carrying the larger current, the correct value of current flowing through the circuit and producing a galvanometer deflection in the receiving set equal to the average deflection due to the signal has been estimated from the relation :

$$\text{Correct current} = \frac{R_0}{R} \times \text{apparent current.}$$

By multiplying this correct value of the current by the impedance between the tapping points on the Hull cylinder the correct value of the signal voltage has been obtained.

We shall record below a set of night observations on 28. 3. 37. The day observations of this date have already been entered.

Dacca time.	Changes in galvanometer deflections.
7 P. M.	73, 27, 0, 2, 8·5, 15, 9, 28, 40, 32, 29, 27, 20, 24, 22, 25, 30, 37, 54, 53, 48, 48, 37, 31, 20, x, 7, 15, 9, 8, 5. scale divs.
	Mean : 26·65 scale divs.
7-30 P. M.	10, 32, 24, 35, x, 7, 8, 19, 8. 0, 10, 27, 8, 4. 9, 44, 74, 30, 25, 19·5, 30, 24, 5, 28, scale divs.
	Mean : 21·4 scale divs.
8-8 P. M.	40, 98, 105, 30, 0, 14·5, 14, 22, 37, 11, 17, 20, 0, 52, 79, 86, 35, 28, 68. 54, 3, 23·5, 41, scale divs.
	Mean : 38·5 scale divs.
8-45 P. M.	10, 20, 0, 6·5. 13, 70, x. 155, 117, 113. 56, 45, 1, 10, 2, 8·5, 5, 55, 35, 23, x, 7·5, 1, 23. scale divs.
	Mean : 33 scale divs.

9-45 P. M.   21, 9, 18·5, 40, 45, 29, 75, 54, 110. 23, 7, 26,
                           5, 28, 1, 35, 33, 28, 16, 90, 60, 21, 0, 75, 128,
                           26, 15; 20,   scale divs.

                                      Mean :   23·05 scale divs.

The values of the field-strengths calculated are given in table III.
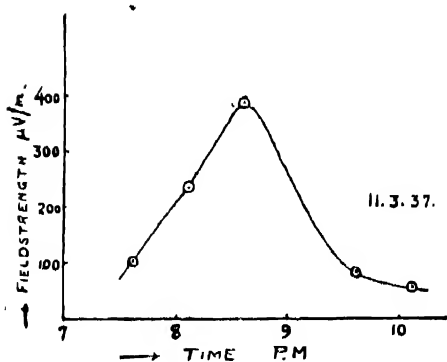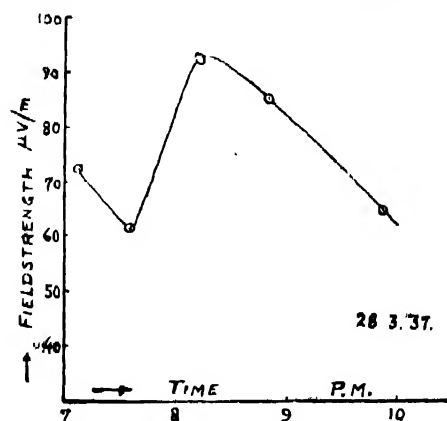
FIGURE 6.

TABLE III.

Mean time	Mean galv. deflection	Mean signal voltage (volt) (i × Z) Z = 14·19 × 10⁻²		Mean field-strength μV/metre
7 — 7½ P. M.	26·65	28·76 × 10⁻⁵ × Z		72·19
7 — 36 P. M.	21·4	24·41 × ,, ,,		61·28
8 — 14 P. M.	38·5	36·69 × ,, ,,		92·17
8 — 51 P. M.	33	33·83 × ,, ,,		84·98
9 — 52½ P. M.	23·05	25·69 × ,, ,,		64·54

The calibration curve showing the changes in the galvanometer deflection for different uncorrected voltages is the same as that constructed for the determination of the day field-strength. (See fig. 4.)

The field-strengths of the night signals from Calcutta on another date (11. 3. 37.) are given in table IV.

TABLE IV.

Mean time	Mean deflection	Mean signal voltage (volt) $(i \times Z)$ $Z = 14 \cdot 19 \times 10^{-2}$	Mean field-strength μV/metre
7·37½ P. M.	21·3	$4 \cdot 1 \times 10^{-4} \times 14 \cdot 19 \times 10^{-2}$	103
8—7½ P. M.	50·7	9·35 ,, ,, ,,	234·8
8—37½ P. M.	92·7	15·5 ,, ,, ,,	389·3
9—37½ P. M.	15·7	3·2 ,, ,, ,,	80·4
10—7½ P. M.	10·7	2·3 ,, ,, ,,	57·8

These results are shown in figure 6.

The field-strengths of the night signals from V. U. D. (Delhi) station ($\lambda = 340 \cdot 13 \, m$) received at Dacca have also been measured. The values are given in table V.

TABLE V.

Date. 19th March, 1937.

The plane of the loop aerial makes an angle of $57° \cdot 8$ with the Delhi-Dacca direction. $E = 1 \cdot 96 \, V$ volts/m. $Z = 15 \cdot 42 \times 10^{-2}$

Time	Mean Galv" divisions	Mean signal voltage along loop plane	Field-strength along loop plane	Field-strength (mean)
7-42 P. M.	12·47	$1 \cdot 894 \times 10^{-4} \times Z$	$57 \cdot 38 \mu V/m$	$107 \cdot 5 \, \mu V/m$
8-24 P. M.	19·06	$2 \cdot 261 \times 10^{-4} \times Z$	$68 \cdot 48 \mu V/m$	$128 \cdot 5 \, \mu V/m$

Our thanks are due to the Head of the Department of Physics for all the facilities given during the course of the work.

PHYSICS DEPARTMENT,
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REFERENCE.

[1] Turnbull, J. H., *Q.S.T.*, Jan., 1925; *vide Wireless Engineer and Experimental Wireless*, p. 316 (1925).

[2] Martyn, D. F. *Proc. Roy. Soc., Edin.*, 1930.

FINE STRUCTURE OF THE FIRST SPARK SPECTRUM OF ARSENIC IN THE VISIBLE REGION.

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Plate XIV.

ABSTRACT. The hyper-fine structures in the majority of the stronger lines of the first spark spectrum of arsenic in the visible region have been measured and analysed. The source used was a hollow-cathode discharge tube containing arsenic in which helium was continuously made to circulate at a low pressure. The structures have been measured by means of a quartz Lummer plate in conjunction with a Hilger's glass spectrograph. The analysis has definitely shown that the nuclear spin of arsenic is 3/2.

The terms investigated are those belonging to $4s^2\,4p.5s$. and the $4s^2.4p.5p$. electron configurations found in most of the lines in the visible region. Fine structure interval factors have been calculated for 14 terms belonging to the above electron configurations. In addition, the structures of the terms $sp^{33}D_2$ and $sp^{33}D_3$ have been determined. The structures of the terms $4d.^1D_1$, $4d.^3D_1$, and $4f.^3F_2$ have also been estimated

The fine structure analysis also confirms the gross structure analysis.

INTRODUCTION.

In a recent communication[1] the hyper-fine structure of a few lines in the first spark spectrum of arsenic has been discussed, and it has been shown that the nuclear spin of arsenic is 3/2, as previously proposed by S. Tolansky.[2] He had studied the visible region of the As II. lines using a silvered Febry-Perot interferometer. The source used by him was a simple quartz Geissler tube with thick iron rods as electrodes. The tops of the electrodes were covered with powdered arsenic and pure helium was circulated continuously through the tube at a low pressure. The tube was excited by means of a transformer and the observations were made end on. He measured the fine structures of the strong visible lines of As II. and showed that the structures could be explained by taking the nuclear spin of arsenic as 3/2. This region has also been investigated by A. S. Rao[3] by using a quartz Lummer plate. But some of his results are so widely divergent from that of Tolansky that it was considered worth while to re-investigate the entire glass region from λ 7000-4300Å.

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The efficiency of a hollow-cathode discharge tube as a source for studying the fine structures of lines being well known it was decided on the present occasion to produce the As II. spectrum in a slightly modified form of Schüler's water-cooled hollow cathode discharge tube. The details of this arrangement, which gave excellent results are given later. In this investigation in all about 20 As II. lines have been examined for fine structure, and the analysis has been made by the usual constant frequency difference method in the case of well resolved lines showing simple structures. Some of the lines have been found to be complex and incompletely resolved. The Fisher-Goudsmit[4] graphical method of analysis has been employed in the analysis of such lines. In the analysis of lines with complex structures this method has been found to be extremely useful and therefore a brief description of this method is also given later. The gross-structure multiplet analysis of As II. lines have been made by A. S. Rao[5] and his line classifications have been employed here. The terms investigated are those belonging to $4s^2.4p.5s$ and the $4s^2.4p.5p$ electron configurations found in most of the lines in the visible region. The structures of the terms previously obtained by S. Tolansky (*loc. cit.*) and A. S. Rao (*ioc. cit.*) from lines in the visible region have been re-determined. They have also been checked from quite independent data obtained from the investigation of the As II. lines made by the author in the ultra-violet region. Fine structure interval factors of all these terms have also been calculated. The fine structures of a number of terms have also been checked wherever they were found involved in two or more line transitions the structures of which were known or previously determined.

APPARATUS.

For hyper-fine structure work it is important that the source of light should be free from the causes that produce broadening of the spectral lines. The usual sources such as the flame, arc, spark or a Geissler tube, all suffer from the defects that they are not free from the Stark and Doppler broadening effects and hence they are not suitable for work of this nature. The experimental use of the hollow cathode source is well known and has been almost commonly used for this kind of work in recent years. Paschen[6] had shown that the source could be adapted also for metals of low melting points or those which, like arsenic, vaporise quickly. In such a case he found that the metal in question could be placed in a carbon or tungsten hollow cathode. In the present investigation an iron hollow cathode tube of the form designed by Paschen[7] and modified by Schüler, about 7 cm. long and 1 cm. in internal diameter, as described in the previous communication, (*loc. cit.*) was used. The anode, made of thin sheet of aluminium, was a co-axial cylinder, of the same diameter as the cathode, or it was a brass tube separated from the cathode by means of pyrex. The top of this tube had a circular opening ground and planed and closed with a window

The cathode and the anode were both water-cooled by covering both of them with spirals of brass tubings through which cold water was continuously made to flow throughout the course of the experiment. Pure dry helium was taken in a globe of glass and this was connected with the apparatus by means of suitable taps by means of which a small quantity of helium could be admitted into the system for circulation throughout the experiment. The liquid air cooled traps used in the experiment served to absorb mercury vapour and other impurities. Exposures were begun only after all the impurities were absorbed, which took several hours, sometimes even over twenty-four hours when a freshly made cathode is used. A quartz tube containing copper-oxide was included in the circuit. This was heated when necessary in order to absorb the hydrogen. Two pumps were included in the system. The first was a hyvac rotary pump which served to exhaust the whole system to a hard vacuum. The second was a mercury vapour two stage pump which when set in action served to keep the admitted quantity of helium in circulation in the whole system including the hollow-cathode discharge tube. A small gauge was included in the circuit to register the pressure of this helium gas. It may be noted here that instead of the usual charcoal a mineral known as chabazite was used in the liquid air cooled traps. This chabazite as an absorbent in place of the usual charcoal has the advantage that it does not absorb helium in any large proportion, so that the helium supply to the discharge has not to be renewed too frequently. It was used throughout the course of the experiments. The fine structures of the lines were examined by means of a quartz Lummer plate in conjunction with a Hilger E 2 spectrograph using the glass train for the visible and the near infra-red region. A diagrammatic sketch of the apparatus used is given in figure 1.
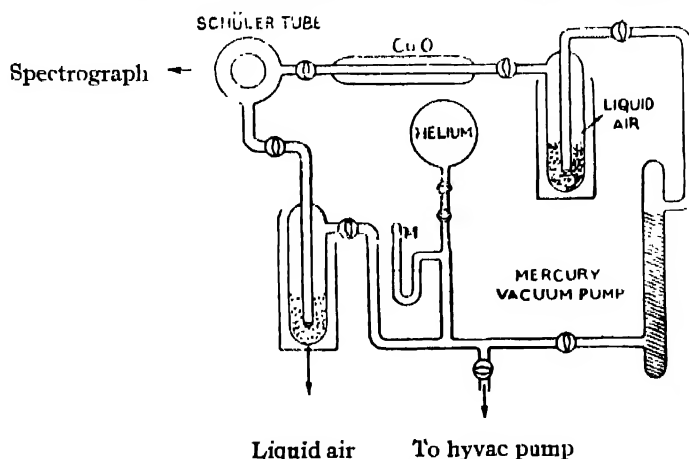

FIGURE 1.

EXPERIMENTAL.

To start with, the whole system was exhausted to a hard vacuum, the pump being worked for hours together till the impurities were absorbed by the traps,

the copper-oxide tube being also heated at the same time, if necessary, to absorb the hydrogen, faint traces of which are usually present as an impurity in the helium supply and in the various parts of the apparatus, and till there was a general clean up of the whole system as observed through a direct-vision spectroscope. The hydrogen line then at the same time almost completely disappeared. Helium was then gradually introduced into the system till the gauge indicated a pressure of about one millimeter. The mercury vapour pump was then set in action and this served to keep the admitted quantity of helium in circulation throughout the experiment. As regards getting a brilliant spectrum of arsenic the device employed was the same as that described in the author's previous paper referred to above. Ilford hyper-sensitive Panchromatic plates, speed 2500 were used for photographing the spectra, and exposures varying from two to eight hours were found necessary for the entire region in the visible and the near infra-red portions of the spectrum. The temperature of the room was nearly constant during this interval, and only those plates were measured during the exposure periods of which the barometric pressure variation was negligible and the line structures were fairly sharp, as during the long hours of exposure the temperature and pressure of the air do not always remain constant and thereby the fringes get displaced considerably, becoming useless for any reliable measurement.

Table I gives a complete list of the lines studied for fine structures. The strongest component of each line is taken as the main or null line and the separations of the rest are given in units of $cm^{-1}.10^{-3}$. The visually estimated intensities of the components are given below each of them in brackets. Structures are classed as A, B and C according to whether resolution is good, medium or poor. The poorly observed components are mostly blurred patches incompletely resolved by the instrument. Most of the lines were found regular, the components degrading to the violet both in intensity and interval, but a few lines showed an inverted structure, that is, their components were found degrading to the red. This was also found to agree with the analysis given later. The lines which have shown a complex structure have been analysed by the graphical method of Fisher and Goudsmit. [8] This method, as will be seen later, has been found extremely useful in the analysis of such lines.

It will be seen that in table I given below the observations recorded by Tolansky and by Rao in the region investigated by them have also been added for the sake of comparison.

Table II gives a list of lines which either show no structure or are blurred narrow patches of light or which only show slight broadening indicative of a very small structure not possible to resolve.

TABLE I.

Structures measured in units of $cm^{-1}.10^{-3}$.

Wave-length	Intensity	Classification	This Investigation (Red)	This Investigation (Violet)	Class	Tolansky	Rao
6512·42	4	$5p\,{}^1D_2 - G$			A		
6170·6	10	$5s\,{}^3P_1 - 5p\,{}^1P_1$	115 (5) · 0 (10) · 69 (1) · 119 (1)	54 · 198 (7)	A	118 (5) · 0 (20) · 76 (2) · 124 (2) · 201 (15)	100 (2) · 0 (10) · 80 (1) · 115 (0) · 200 (6) · 0 (10)
6110·3	10	$5s\,{}^1P_1 - 5p\,{}^3P_1$	Single		B	Single	309 (1) · 285 (3) · 200 (6) · 0 (10)
6022·81	10	$5s\,{}^3P_0 - 5p\,{}^1P_1$	218 (1)	136 (2) · 0 (3)	A	198 (1) · 120 (2) · 0 (3)	190 (1) · 120 (2) · 0 (3)
5838·19	9	$5s\,{}^3P_2 - 5p\,{}^3D_3$	Single	0 (3) · 126 (1)	A	...	0 (3) · 86 (2) · 130 (1)
5651·3	10		79 (2)		B	0 (3) · 74 (2) · 112 (1)	0 (3)
5558 31	10	$5s\,{}^3P_1 - 5p\,{}^3D_2$	88 (3) · 0 (10) · 38 (1)	114 (5) · 162 (1)	B	85 (4) · 0 (20) · 37 (5) · 112 (10) · 158 (5)	0 (3) · 40 (2) · 107 (7) · 169 (2)
5497·98	10	$5s\,{}^3P_0 - 5p\,{}^3D_1$	0 (6) · ?		A	90 (2)	0 (3) · 95 (2) · 240 (1)
5385·52	5	$5p\,{}^3P_1 - b$	Single		A	Single	0 (3)
5331·54	10	$5s\,{}^3P_2 - 5p\,{}^3P_2$	0 (6) · 84 (4)	133 (2)	B	88 (2)	90 (2) · 130 (1)
5107·8	10	$5s\,{}^1P_1 - 5p\,{}^1D_2$	0 (1) · 85 (2) · 126 (1)	47 (1) · 157 (1)	C	119 (1) · 41 (1)	0 (3)
5105·8	10	$5s\,{}^3P_2 - 5p\,{}^3S_1$	0 (3) · 190 (2)	302 (1)	C	0 (3) · 95 (1) · 144 (2) · 171 (2)	185 (2) · 285 (1)
4985·6	8	$5s\,{}^3P_1 - 5p\,{}^3P_1$	Single		A	194 (2) · 311 (1)	210 (0) · 650 (2)
4888·74	8	$5s\,{}^3P_0 - 5p\,{}^3P_1$	Single		B	Single	0 (3)
4730·92	10	$5s\,{}^1P_1 - 5p\,{}^3P_2$	0 (3) · 134 (2)	231 (1)	B	0 (3) · 139 (2) · 230 (1)	125 (2) · 200 (1)
4707·82	10	$5s\,{}^1P_1 - 5p\,{}^1S_0$	Single		B	Single	82 (2) · 140 (1)
4458·7	7	...	0 (6) · 397 (4)	625 (2)	B	...	0 (3)
4431·73	10	$4d\,{}^3D_1 - 4\,{}^{f3}F_2$	Single		A	0 (4) · 276 (3) · 513 (2) · 666 (1)	100 (10) · 260 (7) · 480 (5) · 635 (3)
4371·38	8	$5p\,{}^{33}D_3 - 5p\,{}^3D_3$	0 (4) · 288 (3) · 512 (2)	68 (1)	A		
4336·89	9	$5p\,{}^3D_2 - 5p\,{}^3D_1$	0 (4) · 159 (3) · 274 (3)	341 (1)	A	0 (4) · 159 (3) · 274 (2) · 341 (1)	0 (4) · 170 (2) · 290 (1)

TABLE II.

Wave-length.	Intensity.	Classification.	Remark.
6512·42	(4)	$5p^1D_2 - G$	Narrow
6110·3	(10)	$5s^1P_1 - 5p^3P_1$	Broad
5838·19	(9)		Single
5385·52	(5)	$5p^3P_1 - b$	Single
4888·74	(8)	$5s^3P_0 - 5p^3P_1$	Single
4707·82	(10)	$5s^1P_1 - 5p^1S_0$	Single
4466·60	(9)	$4d^1D_2 - F$	Single
4431·73	(10)	$4d^3{}_1D - 4f^3F_2$	Single
4427·38	(10)	$4d^1P_1 - C$	Single
4324·1	(8)	$5p^3P_0 - c$	Single
4315·86	(8)	$sp^{33}D_1 - 5p^3D_1$	Broad & Hazy
4302·26	(3)		Single

ANALYSIS.

The Fisher-Goudsmit method of analysis which has been frequently employed here has been found to be very useful in the analysis of complex and incompletely resolved structures and so it is briefly given here. —

At first the complete multiplet is drawn with the interval factors of both the upper and lower terms equal. The resulting line structures are then plotted as points along a straight line, say, AB. The upper term is then completely inverted and keeping the interval factor unchanged, the new multiplet formed is again drawn as points along another parallel straight line, say, C D, below the first line. The lines involving identical F transitions are then joined by straight lines whose breadths are made roughly proportional to the intensities of the transitions as calculated from Hill's [9] formula or directly obtained from the Relative Intensity Tables of White and Eliason.[10] It is evident then that at the upper limit the pattern will be that given when the interval factor ratio of the two terms is $+1$ and at the lower limit when it is -1. The centre pattern, which is along a line, say, E F, drawn midway between and parallel to A B and C D will then be the pattern formed when the interval factor of the upper term is zero. This diagram can now be used in the interpretation of hyperfine structures of lines, the structure of one level

of which is known, whilst for the other only the F values are known or are sus-pected, and the intervals are unknown. The structure of any line can now be determined for any ratio of interval factors by simply drawing a horizontal line at the point corresponding to that ratio. All that needs be done then is to find out where the measured line fits into the graph and when this is done the values of both the upper and lower interval factors are at once determined although the line pattern is incompletely resolved. The interval rule, in this method, is assumed to hold and so the actual intervals can also be calculated. The detailed analysis of the individual lines and the determination of the structures of the terms will now be considered. The lines have been examined in the order best suited for analysis and the results obtained here have in most cases been checked by examining the structures of more than one line involving common terms. Measurements have also been checked by comparing the observations made of the same lines on different plates. In this investigation advantage has also been taken of the analysis of some lines made by the author in the ultra-violet region the details of which will be found elsewhere, to determine the structures of some terms in the visible region.

$$\lambda 4888{\cdot}74. \qquad 5s^3 P_0 - 5p^3 P_1.$$

This line, as given in table I, has been observed single It has shown no structure on any of the plates. Since the number of fine structure levels of a term is given by $2I + 1$ or $2J + 1$ (where I is the nuclear spin and J the total angular momentum) according to which has the smaller value, so the term $5s^3 P_0$ remains single, since the J value of this term is equal to zero ($2J + 1 = 2 \times 0 + 1 = 1$). Hence it follows that the structure in the term $5p^3 P_1$ is very small and is not measureable.

$$\lambda 4336{\cdot}89. \qquad sp^{3\,3}D_2 - 5p^3 D_1.$$

The analysis of this line has already been given in a previous communica-tion by the author.[11] It is a sharp, perfctly resolved, regular quartet degraded to the violet. It has been shown that the quartet structure of this line is the term structure of the term $sp^{3\,3}D_2$ and that the structure of the term $5p^2 D_1$ must be negligibly small.

$$\lambda 4985{\cdot}4. \qquad 5s^3 P_1 - 5p^3 P_1.$$

This line has been observed as a well resolved regular triplet degrading to the violet. The term $5p^3 P_1$ has already been shown to be single from the analysis of the line $\lambda 4888{\cdot}5$. Hence the triple structure of this line is due to the term $5s^3 P_1$. The interval factor obtained for this term is 76.
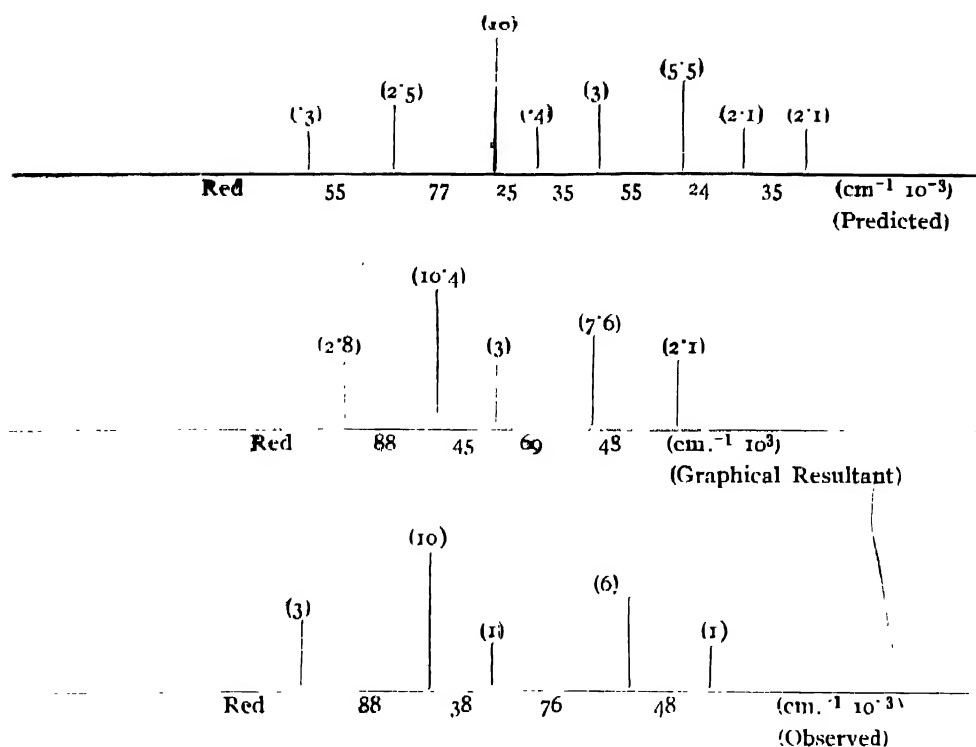
FIGURE 2.

$\lambda 5558'1. \quad 5s\,^3P_1 - 5p\,^3D_2.$

This line has shown a complex structure. Five components at intervals of 88, 38, 76 and 48° have been observed and they do not follow the interval rule. The structure of the term $5s^3P_1$ is already known from the analysis of the previous line. Further verification of the structure of this term has also been ob-

(a)

(b)

(c)

(d)

(e)
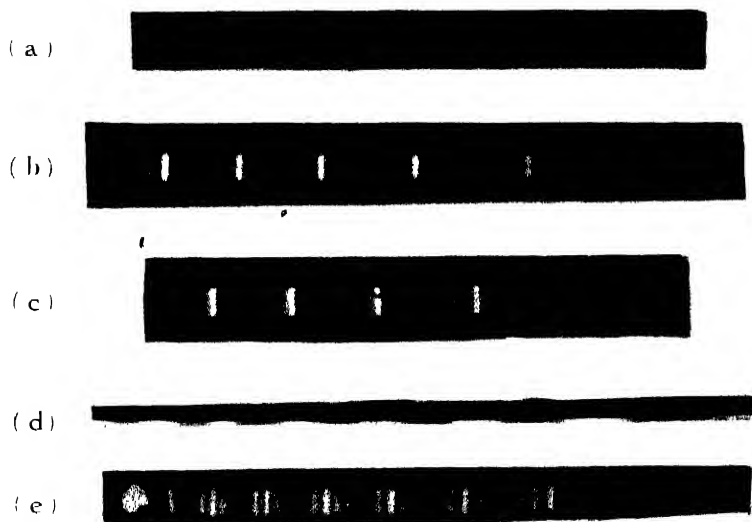
(*a*)   Singlet structure shown by the line λ 6110·3 4*p* 5*s* ¹*P*₁ − 4*p* 5*p* ¹*P*₁

(*b*)   Inverted doublet structure shown by the line λ 5497·98, 5*s* ³*P*₀ − 5*p* ³*D*₁ degrading to the red.

(*c*)   Inverted triplet structure shown by the same line λ 5497·98, 5*s* ³*P*₀ − 5*p* ³*D*₁ degrading to the red.

(*d*)   Quartet coarse structure shown by the line λ 4371·4, *sp*³ ⁴*D*₁ − 5*p* ⁴*D*₂

(*e*)   Quartet structure shown by the line λ 4336·89, *sp*³ ⁴*D*₂ − 5*p* ⁴*D*₁.

tained by the author from the analysis of the line $\lambda 3749\cdot77$. $5s\ ^3P_1 - 5p\ ^1S_0$, in another investigation, in the ultra-violet region, of As II lines. The Fisher-Goudsmit method of analysis can now be employed to determine the structure of the other term, $5p\ ^3D_2$, of this line. The results obtained can then also be checked by the usual method of analysis. It will be seen from the diagram that this line fits into its graph at a ratio of lower to upper interval factors of 100 to 28. The observed intervals are, as mentioned above, 88, 38, 76 and 48 and those predicted from the graph are 88, 45, 69 and 48. As the interval factor of the lower term is already known to be 76, so the interval factor of the upper term is 22 (approx.). The predicted, resultant and observed patterns are shown in figure 2 and the Fisher-Goudsmit diagram is shown in figure 2·(a). It will be seen that the agreement is good.
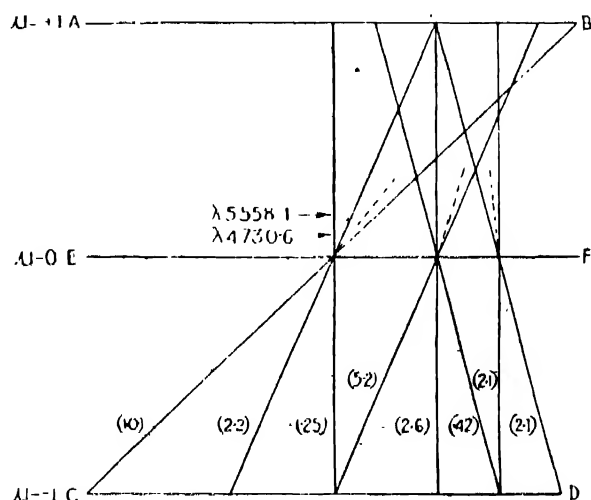
FIGURE 2(a).

$$\lambda 4371\cdot4. \quad sp^3\ ^3D_3 - 5p\ ^3D_2.$$

This line has been observed as a perfectly resolved quartet having a very coarse structure. The components are at intervals of 288, 224 and 169. As the structure of the term $5p\ ^3D_2$ is already known from the analysis of the previous line, the structure of the term $sp^3\ ^3D_3$ can then be obtained. The predicted and the observed patterns have been found to agree remarkably well in both intensity and intervals and the interval factor of the lower term of this line comes out to be 81.

$$\lambda 4730\cdot92. \quad 5s\ ^3P_1 - 5p\ ^3P_2.$$

This line was observed as a triplet with poor resolution the components degrading to the violet. The structure of the term $5s\ ^3P_1$ is already known from

4

the analysis given above. In order to determine the structure of the upper term, $5p\ ^3P_2$, the Fisher-Goudsmit method of analysis can be employed and the ratio of the interval factors of the upper and lower terms of this line can then be determined. Referring to the diagram in figure 2 (a) it will be seen that this line fits into its graph at a ratio of lower to upper interval factors of 100 to 19, that is, 76 to 14. Analysis of the line $\lambda3842\cdot82.\ sp^3\ ^3D_3 - 5p\ ^3P_2$, in the ultra-violet region, made by the author in another investigation has shown that the interval factor of the term $5p\ ^3P_2$ is 14. Hence the agreement is remarkably exact. The analysis of this line, then, affords a check on the analysis of the above lines involving the terms of this line.

$$\lambda6110\cdot3. \quad 5s\ ^1P_1 - 5p\ ^3P_1.$$

This line is single. It shows no structure. Since the upper term has already been shown to be very narrow, the term $5s\ ^1P_1$ must also be small or single.

$$\lambda4707\cdot82. \quad 5s\ ^1P_1 - 5p\ ^1S_0.$$

This line is also single. The fine structure term multiplicity being $2J + 1$ and J being equal to zero, the term $5s^1\ P_1$ must also be small or single.

$$\lambda6022\cdot81. \quad 5s\ ^3P_0 - 5p\ ^1P_1.$$

This line is observed as a regular inverted triplet degraded to red. The term $5s^3\ P_0$ having a J value equal to zero is single. Hence the structure of this line gives the triplet structure of the term $5p^1\ P_1$. In this line the interval rules are exactly followed. The interval factor obtained is 54.

$$\lambda6170\cdot6. \quad 5s\ ^3P_1 - 5p\ ^1P_1.$$

This is a complex line showing five components. The structure of both the upper and lower terms have already been determined from the lines discussed above and hence the analysis can be made. It is found that the predicted and the observed patterns agree reasonably well considering that the third and the

$\lambda5331\cdot53\cdot5s^3P_2 - 5p^3P_2$ $\lambda5105\cdot8\cdot5s^3P_2 - 5p^3D_3.$

Fig. 3(a).
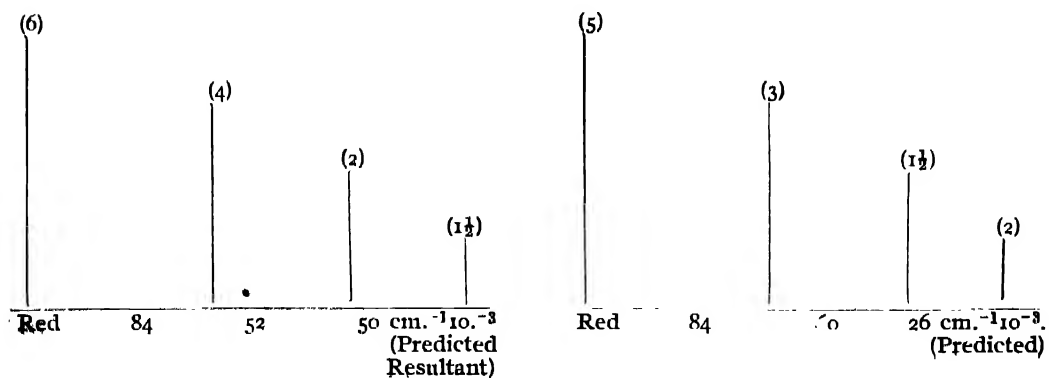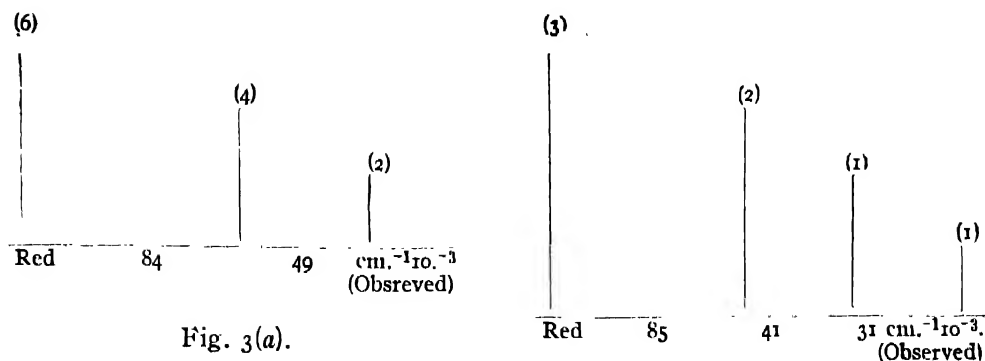
Fig. 3(b).

$$\lambda 5651\cdot3\cdot5s^3P_2-5p^3D_3.$$
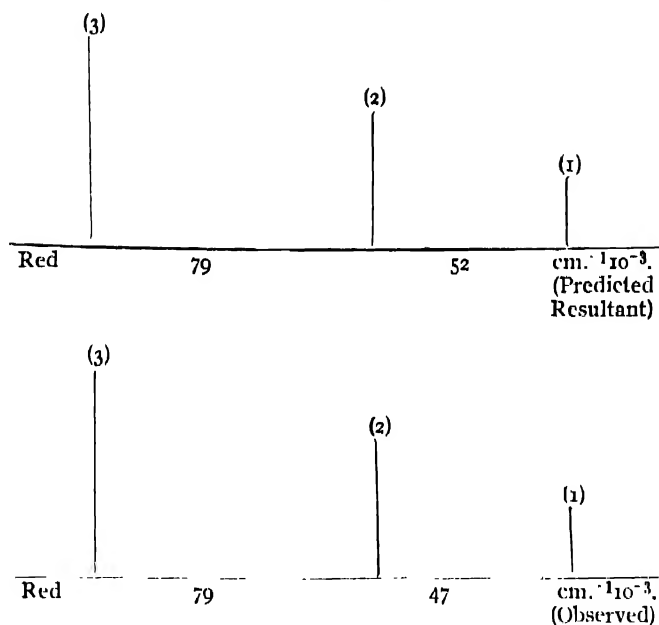
Fig. 3(c).

fourth components of this line were extremely weak and difficult to measure accurately. This analysis, then, also affords a check on the analysis of the previous lines.

$$\lambda 5331\cdot54. \quad 5s^3P_2-5p^3P_2.$$

This line has shown a very narrow and complex structure. Three components only were observed and measured. The interval factor of the term $5p^3P_2$ has already been determined. Hence the structure and the interval factor of the term $5s^3P_2$ can be determined. This line fits into its graph at a ratio of lower to upper interval factors of 100 to 46, indicating that the structures of both

the terms are of similar order. Hence the line structure is complex and difficult to resolve. The analysis is given in figure 3(a), and the Fisher-Goudsmit diagram is shown in figure 4. The agreement is satisfactory but the predicted fourth component is missed. The interval factor obtained for the term $5s^3P_2$ is 31.
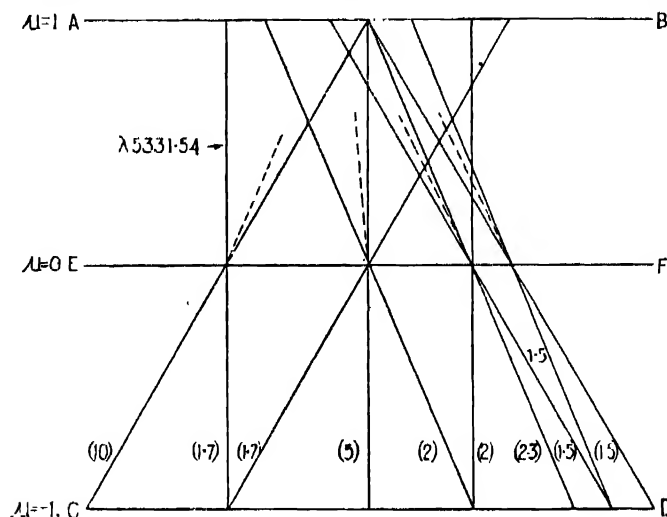
FIGURE 4.

$$\lambda 5105 \cdot 8. \quad 5s^3P_2 - 5p^3S_1.$$

This line has been observed as a very narrow quartet giving extremely poor resolution. The sructure of the term $5s^3P_2$ is already known from the previous line, hence the structure of the term $5p3S_1$ can be determined. But in this case it has been possible only to estimate its value as the resolution is very poor. The best fit of this line into its graph is at a ratio of lower to upper interval factor of 100 to 42. The observed intervals are 85, 41, 31 and those predicted 85, 60 and 26, which is not very satisfactory. The interval factor of the term $5p^3S_1$ should then be 13 which is only approximate. The analysis is shown in figure 3(b), and the Fisher-Goudsmit diagram is shown in figure 5.
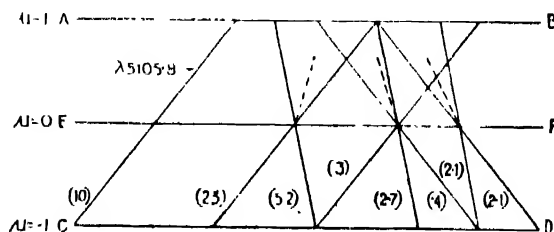
FIGURE 5.

$$\lambda 5651 \cdot 3. \quad 5s^3P_2 - 5p^3D_3.$$

This line is also complex showing three components degraded to the violet. The structure of the lower term is already known from the analysis of the line

$\lambda 5331\cdot 54$. Hence the structure of the upper term can be determined. This line fits into its graph at a ratio of lower to upper interval factors of 100 to 53. Hence the widths of the terms $5s^3P_2$ and $5p^3D_3$ are of similar order giving a complex structure to the line. The interval factor of the lower term is 31 as already determined. Hence the interval factor of the upper term is 16. The analysis is shown in figure 3(*c*) and the Fisher-Goudsmit diagram in figure 6.
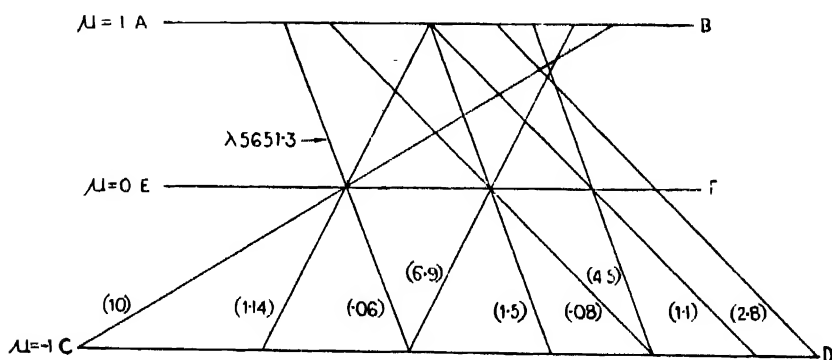
FIGURE 6.

$\lambda 6512\cdot 42$. $5p^1_2D_2 - G$ and $\lambda 5107\cdot 8\cdot 5s^1P_1 - 5p^1D_2$.

These two lines have only shown a broad structure the total widths of which are respectively 54 and 47 units. The term $5s^1P_1$ is already known to be very narrow. Hence the broadening in the line $\lambda 5107\cdot 8$ is due to the term $5p^1D_2$ which is common to both the lines. It follows, therefore, that G is narrow and the slight differences in the widths of these two lines is due to the slight difference in the structures of the terms $5s^1P_1$ and G, which is not possible to resolve. The interval factor of the term $5p^1D_2$ can now be determined and it comes out to be only 7.

$$\lambda 4427\cdot 38, \quad 4d^1P_1 - C.$$

This line has only shown a slight broadening which is evidently due to the term $4d^1P_1$ and hence the term C should be single.

$$\lambda 4324\cdot 1. \quad 5p^3P_0 - e.$$

This line is also observed single. The term $5p^3P_0$ having J value equal to zero is single. Hence the term e is also single.

$$\lambda 5385\cdot 52. \quad 5p^3P_1 - b.$$

This line is single. The term $5p^3P_1$ has already been found single in the line $\lambda 4888\cdot 74$. The term b is, therefore, also single or very narrow.

$$\lambda 4431 \cdot 73. \quad 4d^3D_1 - 4f^3F_2.$$

This line has been observed as a single line with no trace of structure in it. Hence, it is probable, that both the upper and lower terms of this line are single.

It will be seen from table I that the lines $\lambda 6110 \cdot 3$, $\lambda 5407 \cdot 98$, $\lambda 4888 \cdot 74$ and $\lambda 4707 \cdot 82$ have been observed as single by S. Tolansky. But according to Rao all these lines show hyperfine structure. These lines have been examined carefully in this investigation and it has been found as shown in table I that the lines $\lambda 6110 \cdot 3$, $\lambda 4888 \cdot 7$ and $\lambda 4707 \cdot 82$ are single. On none of the plates these lines have shown any structure. Moreover, analysis of other lines, as given above, which involve terms common to these three lines definitely indicate that these lines should have no structure. The line $\lambda 5497 \cdot 98$. $5p^3P_0 - 5p^3D_1$ has invariably shown two strong components degraded to red on most of the plates while one plate has definitely shown three components degraded in intensity and intervals to the red. The term $5p^3D_1$ should then be a triplet, as is demanded by a term with J value equal to one if the line concerned actually shows any structure. But the analysis of the lines $\lambda 4336.89$. $5p^3{}^3D_2 - 5p^3D_1$, $\lambda 4190.37 \cdot$, $5p^3D_1 - d$, and $\lambda 3720.31$. $5p^3D_1 - f$, which have the $5p^3D_1$ term in common, has shown that this term should be single. Hence it is possible that the doublet and the triplet structures observed in this line may be either due to some impurity or due to some line or lines of the second spark spectrum of arsenic of very nearly the same wave-length. Unfortunately no further tests could be made for want of a second Lummer plate with a different thickness. It is interesting to note here that these components have followed the interval and intensity rules.

As will be seen from the analysis the term structures have often been determined from more than one line. Simple lines have generally followed the interval and intensity rules fairly accurately. But in the case of complex lines this could not be tested since Fisher and Goudsmit's method of analysis involves the assumption that the interval rules are strictly followed. No lines of any measurable strength in the Arsenic II spectrum lie in the region $\lambda\lambda 7000 - 6500$. Over eight hours of exposure with hypersensitive Panchromatic plates further sensitised in a dilute ammonia bath and rapidly dried has not shown any arsenic lines of measurable strength. A few lines investigated here have only been partially allocated. The term structures of such lines have, therefore, only been estimated.

The structures and interval factors of the various terms investigated are given in table III. The interval factors of the terms investigated by Tolansky and by Rao have also been given in the 4th and 5th columns of this table for a comparative study. It will be seen that the results of Tolansky agree remarkably well with the present investigation but some of Rao's results recorded here show wide divergence.

TABLE III.

Term Fine Structures and Term Interval Factors.

Terms		Fine Structure Intervals	Term Interval Factors		
			This Investigation	Tolansky	Rao
5s	$^3P_0$	Zero	Zero	Zero	Zero
	$^3P_1$	190, 112	76	78	76
	$^3P_2$	109, 78, 47	31	33	29
	$^1P_1$	Small	Small	Small, Inverted	33
5p	$^1S_0$	zero	Zero	Zero	...
	$^3S_1$	33, 20	13	14	...
	$^1P_1$	136, 82	54	50	48
	$^3P_0$	zero	Zero	Zero	Zero
	$^3P_1$	Small	Small	Small	Small
	$^3P_2$	49, 35, 21	14	13	12
	$^1D_2$	...	7(estimated)	12	...
	$^3D_1$	Small	Small	...	...
	$^3D_2$	77, 55, 33	22	24	26
	$^3D_3$	72, 56, 40	16	...	4
sp^3	$^3D_2$	159, 115, 67	46	46	6
	$^3D_3$	365, 283, 202	81	80	78
4d	$^1D_2$	Small	Small	...	...
	$^3D_1$	Small	Small	...	...
4f	$^3F_2$	Small	Small	...	...

In conclusion I wish to express my thanks to Prof. O. W. Richardson, F.R.S., N.L., in whose laboratory at King's College, London, this work was carried on. I wish also to express my indebtedness to Dr. W. E. Williams for the help, advice, and facilities he gave me during the course of this work. I am also grateful to the High Commissioner of India for the award of a substantial grant-in-aid during the course of this work.

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MAGNETIC PROPERTIES OF TELLURIUM ON COLLOIDALISATION.

By MATA PRASAD

AND

S. S. DHARMATTI.

An examination of the literature on the magnetic properties of colloidal powders of metallic elements reveals the fact that there is an apparent change in the diamagnetic susceptibilities of small particles obtained either by mechanical or chemical colloidalisation or by cold working. The problem whether the change is due to (*i*) the fineness of the particle size or (*ii*) the change in the crystal structure brought about by the forces employed or generated in the process of powdering or colloidalisation, or (*iii*) the impurities coming in, due to oxidation, hydration, carbonisation, etc., has engaged the attention of many workers.

Regarding an atom as containing electrons moving in orbits about a centre of force, these orbital electrons providing the molecular currents of Weber, Langevin[1] obtained an expression for the atomic diamagnetic susceptibility which involves besides e, m and c, n the number of electrons in the atom and r^2 the mean square of the radius of the projected orbit in a plane perpendicular to the field. The diamagnetic susceptibility of any element should thus be independent of temperature as well as of the physical state of the element. But the literature shows that different workers have divergent views.

Rao[2] has advanced the view that the magnetic susceptibility is influenced by the particle size and according to Bhatnagar[3] his researches can be divided in the following three classes :—

(1) Bismuth and antimony the diamagnetism of which decreases on colloidalisation. These elements show extraordinarily high diamagnetism an explanation for which can be given on the hypothesis of Ehrenfest.[4]

(2) Copper and zinc the diamagnetic susceptibility of which increases on colloidalisation so that the effect is the same as that of cold working.

(3) Selenium which should not show any change of susceptibility on colloidalisation.

Bismuth, antimony,[5] copper, lead, sulphur, selenium and tellurium[6] have also been investigated by Bhatnagar and collaborators and their experimental

results do not justify any classification. They uphold the view that there is no influence of the size of the particles on the susceptibility of metals. The factors which influence the magnetic properties of the metals are (*i*) the impurities in the form of oxide, hydroxide or carbonate which are rapidly formed when a large surface, on colloidisation of metals, is exposed to air, (*ii*) a change in the crystal structure of the metal and (*iii*) the formation of an allotropic modification of the metal due to large pressures and temperatures developed during grinding or arcing.   A critical and elaborate survey of the whole subject regarding the anomalous diamagnetism and particle size has been given by Lessheim[8] who from the existing experimental evidence concludes that there should be no change in the diamagnetic susceptibility of metals on colloidalisation or cold working.

Prasad and Dharmatti[9] have shown that no change in selenium takes place due to a decrease in the size of the particles by powdering or on colloidisation. A definite change observed by them has been shown to be due to the conversion of selenium into an allotropic modification which differs in density, colour and appearance from the original selenium. The above-mentioned conclusion has been supported by the calculations made on the basis of Honda and Shimizu's theory. Authors take this opportunity of thanking Dr. S. S. Bhatnagar, O.B.E., D.Sc., who suggested the possibility of the formation of allotropic form of selenium under conditions described in the aforesaid publication.

<center>E X P E R I M E N T A L</center>

The magnetic susceptibility was measured by a magnetic balance of the Curie-Wilson type which depends on the torsion method and which was used in our previous work on selenium. The experiment carried out can be divided into the following different parts :—

(1) Powdering tellurium for about twenty-five hours within about a week.

(2) Powdering tellurium for about the same period in about two months.

(3) Powdering tellurium under paraffin for about 25 hours within about a month, washing the powders with ether and alcohol and then drying them under vacuum.

(4) Fusing one of the powders into a lump.

(5) Washing some of these powders with cold dilute hydrochloric acid several times until a constant value for their susceptibilities is obtained.

<center>I.</center>

Kahlbaum's purest sticks of tellurium ($\chi = 0.32 \times 10^{-6}$) were powdered in air in an agate mortar free from any ferrogeneous materials. After powdering

for a definite period a small sample was taken out and its magnetic susceptibility was measured. The remaining powder was further ground and a part of it was again tested. In this manner the susceptibility of a number of specimens powdered for different intervals was measured. The results obtained are given in table I.

TABLE I.

Period of powdering.	$\chi \times 10^6$.
5 Hours	$-0\cdot315$
10 Hours	$-0\cdot295$
15 Hours	$-0\cdot290$
25 Hours	$-0\cdot241$

The average size of the particles of 25 hours' powder was measured. The powder was suspended in propyl alcohol and well shaken. Some drops of this suspension were placed under a high power microscope and the dimensions of about 25 particles were measured by means of a small scale provided in the eye-piece of the microscope and calibrated by a stage micrometer. The mean of all these values comes out to be $0\cdot55\mu$.

II.

Tellurium was powdered in the same agate mortar for about an hour a day so that each of the powders in table II has taken about a week or even more in some cases.

TABLE II.

Period of powdering.	$\chi \times 10^6$.
10 Hours.	$+ 0\cdot0047$
15 Hours.	$+ 0\cdot0527$
20 Hours.	$+ 0\cdot170$
25 Hours.	$+ 0\cdot216$

The average size of the particles of the 25 hours' powder is $0\cdot5\mu$. It is clear that there is a tremendous effect of air since the ten hours, powder in the first series

of experiments is diamagnetic while that in this case is paramagnetic. Ten hours' powdering in this case was finished in about a fortnight.

In order to see whether the impurities entering into the powders could be removed by washing, ten hours' powder was washed with absolute alcohol and was thoroughly dried in a vacuum dessicator and its susceptibility was measured. The value obtained was $+0.014 \times 10^{-6}$ which is a little more paramagnetic than before it was washed ($+0.0047 \times 10^{-6}$). This leads to the conclusion that the impurities, probably in the form of some complex oxides, are not at all soluble in alcohol.

III.

In order to check the influence of air in the formation of simple or complex oxides tellurium was powdered under paraffin. Table III gives the results obtained.

TABLE   III.

Period of powdering.	$\chi \times 10^6$.
5 Hours.	-0.297
10 Hours.	-0.291
15 Hours.	-0.278
25 Hours.	-0.242

It is clear from the table that even after avoiding the influence of air, there is a decrease in the magnetic susceptibility with the reduction in the size of the particle. The average size of the particle of 25 hours' powder is 0.55μ which is very nearly the same as that obtained in the former case (0.5μ *vide* table II). However there is a vast difference in the values of magnetic susceptibilities—one is paramagnetic and the other diamagnetic.

IV.

Since after avoiding the influence of air there is still a decrease in the magnetic susceptibility, one is apt to believe that the size of the particles would influence the magnetic susceptibility. If the size effect is genuine then if the same powder is fused, it must regain the ' en mase ' value. So the powder of 25 hours (table III) was fused and its magnetic susceptibility was measured. Its value was -0.2987×10^{-6} which is a little less than that of the powder (-0.24×10^{-6}). This shows that there is no size effect.

V.

To see whether some impurities are present in the powders they were washed with cold dilute hydrochloric acid, dried in a vacuum dessicator and their susceptibilities were determined. The results obtained are shown in the following table :

TABLE IV.

Specimen.	$\chi \times 10^6$ before washing with HCl.	$\chi \times 10^6$ after washing with HCl.		
		1st wash.	2nd wash.	3rd wash.
From table II 25 hours.	+ 0·216	+ 0·014	− 0·149	− 0·304
From table III 25 hours.	− 0·242	− 0·310		

The above results show that the paramagnetic impurities are almost completely removed by treating the tellurium powders with cold dilute hydrochloric acid and that the powders practically regain the original value for tellurium sticks. The only point that deserves to be noted is that the powder prepared in air requires more washing, indicating thereby that the impurities due to air do come in layers, during powdering.

DISCUSSION OF RESULTS.

The above results are in agreement with those of Bhatnagar and co-workers that the size of the particle has no bearing on the change in the susceptibilities of tellurium on colloidalisation. The very fact that as the time taken for powdering tellurium in air for the same number of hours is increased, the diamagnetic susceptibility not only decreases, but the powders actually become paramagnetic (difference in the susceptibility of the two powders of 25 hours, one prepared within about a week and the other within about two months, is very great) clearly indicates that the change is due to impurities which are formed by the absorption or adsorption of gases resulting in the formation of complex oxides soluble in cold dilute hydrochloric acid.

On the assumption that powdering under inert liquids like paraffin prevents the oxidation effects one should not expect any change in the powder prepared

under paraffin.   But we do find that   there is a fall in diamagnetism.   If this fall
could be attributed to the particle size, the powder, after fusing should regain the
' en mase ' value which does not happen.

It is quite evident from the fact that the paramagnetic and diamagnetic
powders regain the ' en masse ' value after frequent washing with cold dilute
hydrochloric acid that the observed changes are due to impurities which are intro-
duced during powdering.

Authors are thankful to Dr. S. S. Bhatnagar, O.B.E., D.Sc., F.Inst.P.,
for his suggestions.

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ON POSSIBLE ELECTRONIC TRANSITIONS IN Pr^{+++} IONS AND THE ABSORPTION SPECTRA OF THE SAME IN SOLUTION AND IN CRYSTALS.*

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Plate XV.

ABSTRACT. The absorption spectra of Pr^{+++} ions in solution and in crystals have been investigated here over the region from 900 mμ to 200 mμ. In solution the intensity of absorption has been measured over the visible region with a double monochromator. Using large single crystals of PrCl$_3$, 7H$_2$O, the changes brought about at liquid air temperature in the nature of the different groups of absorption lines and bands have been studied. A preliminary classification of these groups of absorption lines and bands is given based on the assumption that they are due to inner forbidden transitions. Every transition is supposed to give rise to a group. In this process of classification the term values of Pr IV have been calculated from those of La II and compared with the mean frequencies of the different groups obtained in absorption The Van Vleck's theory of the absorption spectra of rare earths in solids has been discussed. A scheme of classification of the rare earth spectra presented by Ellis has been noted and the divergences explained.

INTRODUCTION.

In a previous paper [1] the absorption spectra of Nd^{+++} ions in solution and in crystals were investigated by the writer over a wide range of temperature. A classification of the groups of sharp absorption lines and bands, obtained with large single crystals at low temperature, was also attempted there. It was shown that the groups of sharp lines and bands originate from the forbidden transitions inside 4f-shell. The finer structure inside each group, due to the decomposition of the energy levels in the crystalline field as well as to the superposition of the lattice vibrations, was not taken into consideration. The object of the present paper is to report the results of a similar investigation carried on with Pr^{+++} ions in solution and in crystals. It is intended also to classify their spectra broadly.

P. C. Mukherji

EXPERIMENTAL INVESTIGATIONS.

(a) The investigations were precisely similar to those described in the case of Nd^{+++} ions. The absorption spectra of the ions in solution were investigated from 900 mμ to 200 mμ. But in the present case the sharp lines and bands were found to be limited to the visible region. This is due to the fact that Pr^{+++} ions do not possess any sharp absorption spectra in the ultra-violet; in the infra-red they lie beyond 900 mμ up to which it was possible to photograph with the plates available here. In all there were five bands, a double band on the red side and three bands in the blue and violet.

The quantitative study of the absorption of Pr^{+++} ions in solution was carried out with a Hilsch double monochromator, a K-photo cell and a Wulf's string electrometer. The investigation was limited to the visible region only. The results of the measurement are given in table I. A curve showing the variation of the percentage of absorption with wave-length is given in figure 1.

TABLE I.

(Positions of the absorption maxima obtained with the double monochromator.)

	Concentration	Thickness.	Position of absorption maxima.	P. c. of Absorption.
(a)	15%	1 cm.	5970 Au.	14·5
(b)	,,	,,	5855 ,,	22
II	,,	,,	4832 ,,	28·5
III	,,	,,	4684 ,,	38
IV	,,	,,	4436 ,,	57·2

(b) The investigation of the absorption spectra at low temperature was carried out with large single crystals of $PrCl_3, 7 H_2O$. The crystals were prepared in the laboratory by slow evaporation of the saturated solution as described in the previous paper, when very fine hexagonal crystals were obtained. They were ground to different thicknesses and sealed in glass cells. A Hilger E$_1$ spectrograph with glass optical parts was used. The spectra were photographed at the room temperature and at that of liquid oxygen. At the low temperature the exposure varied from 15 to 25 minutes using "Kodak Superpan Cutfilms."

It was found that at the temperature of liquid oxygen the diffuse double band on the red side was resolved into a large number of extremely sharp lines

Absorption Spectra of ($PrCl_3$, 7 H_2O) crystal in the visible region.

(a)   at room temperature
(b)   at liquid air temperature
(a') at room temperature with thicker crystal

and bands. The three bands in the blue and violet regions did not show such extremely fine structure. The first two of these three bands were decomposed into a number of rather diffuse narrower bands, while the third band in the violet remained unaffected. They perhaps require still lower temperature for getting resolved into extremely sharp and narrow components. The thickness of the crystal used was 1.5 m.m. In order to investigate still weaker components, if there be any, a crystal of thickness 3 m.m. was used. It was found that a few weaker components were added to the group of absorption lines in the red. A new group of very faint lines also appeared in the green region. These are shown in plate XV, and the wave-lengths and wave-numbers of these lines and bands are given in the table II.
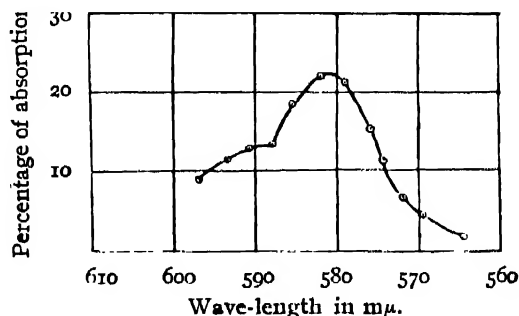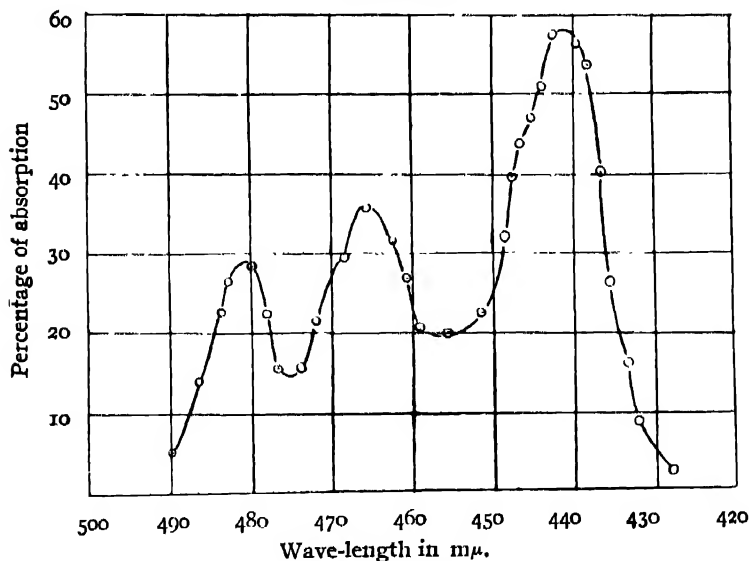

FIGURE 1(a).

FIGURE 1(b).

DISCUSSION OF RESULTS.

It is apparent from the table II that Pr^{+++} ions show five groups of absorption lines and bands in the visible region. Over and above these five groups, there are three groups in the infra-red which it was not possible to photograph

6

TABLE II..

(The wave-lengths and wave-numbers of the lines and bands obtained with single crystals at different temperatures.)

Room Temp.	Oxygen Temp.		Remarks.
λ (Å)	λ (Å)	ν (Cm⁻¹)	
I (a) 5993.5—	5991.1	16,686 8	At the temperature of liquid oxygen the diffuse band is resolved into several narrow and sharp components. The intensity of absorption increases.
5972.1	5984.1	16,706.3	
	5981	16,715.0	
	5955.2	16,787.4	
(b) 5935·4—	5946.1	16,813.1	
5884.9	5938.2	16,835.5	Do.
	5927.8	16,865	
	5903.2	16,935.3	
(c)	5838.5	17,122.9	The three faint and rather diffuse lines split up into sharp doublets and some new lines appear.
	5830.5	17,146.4	
	5800.7	17,234 5	
5795.7	5794.8	17,252.1	
5768	5773.9	17,314.5	
	5759	17,359.3	
5744.6	5753.7	17,375.3	
II	5736.1	17,428.6	
	5263.9	18,992.1	
	5234·6	19,098·4	
5230.9	5229.4	19,117.3	Do.
5215 4	5215·8	19,167.2	
	5200.5	19,223·6	
III	4878.9	20,490.7	The broad band is resolved into narrower bands, but they remain slightly diffuse even at the low temperature.
	4864.5	20,551.4	
4845.9—	4847.1	20,625.2	
4833.8	4843.7	20,639.6	
	4841.2	20,650 3	
	4834 6	20,678.5	
	4826.3	20,714	
IV	4719 2	21,184.1	
4715.2—	4713.2	21,211.1	
4703.4	4707·3	21,237.7	
	4696.6	21,286.1	Do.
4692.5—	4689.5	21,318.3	
4682.8	4670.4	21,405 4	
V 4431.0—	4434—	22,597—	
4473.4	4478	22,325	The band remains un

here. The first two of these were first investigated in solution by P. Lueg[2] using a thermopile and a galvanometer and were found at 2μ and 1.54μ. Later Freyman and Takavorian[3] observed the third in the near infra-red with a thalofide cell· It was found to be a weak band having its crest at 10,182 Å. Gobrecht[4] made precision measurements of these bands using borax beads containing the borate of the element. He photographed the third group on specially prepared infra-red sensitive plates and obtained a number of sharp weak absorption lines using crystals of $Pr_2(SO_4)_3$, $8H_2O$. The centre of gravity of ·each of these groups as well as those observed here are given in table III. The relative intensities of the groups are also noted there.

TABLE III.

(The positions of the centres of gravity of all the different groups observed
in Pr^{+++} ions.)

	Intensity.	C. G. of different groups	Nature.
I	Strong	5,200 cm^{-1}	A broad band.
II	Very strong	6,950 ,,	Possesses some structure.
III	Weak	9,835 ,,	Consists of sharp components at low temperature.
IV (i)	Strong	16,811 ,,	Do.
(ii)	Fair	17,275 ,,	Do.
V	Very weak	19,107 ,,	Do.
VI	Strong	20,602 ,,	Components are diffuse at low temperature.
VII	Strong	21,294 ,,	Do.
VIII	Very strong	22,461 ,,	One broad band.

A preliminary classification of these eight groups of absorption lines and bands will be attempted here on the supposition that they are due to the transitions of the $4f$-electrons inside the $5s$, p-shell. Van Vleck [5] discussed the origin of the spectra of the rare earth ions in solids and showed that their extremely sharp nature and the very feeble intensity could be explained on the assumption that they are due to the inner forbidden transitions. The different possibilities of such transitions as enumerated by him will be referred to later. In Pr^{+++} ions containing two $4f$-electrons the different inner states allowed by Russell-Saunders coupling are given by $^3(P, F, H)$ and $^1(S, D, G, I)$. The ground state according to Hund's rule is given by $^3H_4$; it also explains the magnetic properties of the ion. It now follows from above that electronic transitions between the ground state and the other allowed states give rise to the different groups of absorption bands. Further the appearance of all the bands in monochromatic excitation indicates that all transitions take place from the ground state. The multiplicity of lines inside each group, shown by crystals at low temperature, is taken to be an effect of the crystalline field and also of the coupling of the electronic levels with the lattice vibrations. They will not be discussed here. The C.G's of the groups will instead be regarded as representing the frequencies of the corresponding electronic transitions in absence of any field, and to these the different transitions will be assigned. This will require a knowledge of the relative positions of the different excited levels. According to Hund's rules it follows that among the triplet levels the relative arrangement will be given by $^3P > {}^3F > {}^3H$ and similarly among the singlets. But it is not possible to obtain any relation between the triplet terms on the one hand and the singlet ones having much

higher values of orbital moment on the other.* It is proposed therefore to obtain this information from the evidences of emission spectra.

The emission spectra of Pr IV have not yet been investigated. It is found however that in the analysis of the emission spectra of La II by Meggars and Russell[6] there are several terms to which the electronic configuration $4f^2$ is assigned. These terms are quite analogous to those of Pr^{+++} ions whose transitions are considered here and it seems reasonable to take the relative arrangement of the terms from these data. The values of the corresponding terms of La II together with their symbols are presented in table IV. For convenience, in

TABLE IV.

(Term values of different states of La II with a configuration $4 f^2$.)

Symbol.	J	Term value (cm⁻¹)	$\Delta \nu$	Relative position of terms
^3H	4	55,107·25		0
	5	55,982·09	874·84	874·84 cm⁻¹
	6	56,837·94	855·85	1,730·69 ,,
^3F	2	57,399·58		2,292·33 ,,
	3	57,918·50	518·92	2,811·25 ,,
	4	58,259·41	340·91	3,152·16 ,,
^1G	4	59,527·60		•4,420·35 ,,
^1D	2	59,900·08		4,792·83 ,,
^1I	6	62,408·40		7,301·15 ,,
^3P	0	63,463·95		8,356·70 ,,
	1	63,603·18	139·23	8,495·93 ,,
	2	64,278·92	675·74	9,171·67 ,,
^1S	0	69,505·06		14,397.81 ,,

addition to the absolute term values, their values relative to $^3H_4$ are also given in the table.

Apart from a knowledge of the relative position of the energy levels of Pr^{+++} which is obtainable from these data, it is also possible to calculate their term values. The difference between their values is due to (a) the higher ionisation of the Pr^{+++} ions and (b) the slightly greater value of the effective nuclear charge

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* In the classification of the Nd^{+++} spectra this difficulty did not arise, as the allowed doublet terms with much higher values of L could not be fitted into the scheme of classification on account of their large separations and therefore were not taken into consideration.

of the latter. The effect of these will be to increase the intervals between the energy levels by a constant factor. From a comparison of the separation between the components of the ^3H multiplet, obtained for La II and that calculated in the case of Pr^{+++}, it is found that the factor $\dfrac{2115}{875}$ is approximately 2·41. The values of the different terms of Pr^{+++} ions calculated from those of La II by multiplying with this factor are given in Table V.* The C.G's of the groups observed in absorption are placed side by side with the calculated terms, with which they more or less agree. The changes in L and J occurring in these transitions are given in the last column.

TABLE V.

(Calculated term values of Pr IV and centres of absorption groups of Pr^{+++} ions.)

Symbol	J	Calculated 'ν'	Observed. 'ν'	ΔL ; ΔJ
^3H	4	o		
	5	2,100 cm^{-1}	...	
	6	4,154·4 ,,	...	
^3F	2	5,500·8 ,,	5,200 cm^{-1}	—2 ; —2
	3	6,746·4 ,,	6,950 ,,	—2 ; —1
	4	7,564·8 ,,		
^1G	4	10,608 ,,	9,835 ,,	—1 ; o
^1D	2	11,740·8 ,,	—	
^1I	6	17,522·4 ,,	17,043 ,,	1 ; 2
^3P	o	20,066·8 ,,	20,602 ,,	—4 ; —4
	1	20,390·4 ,,	21,294 ,,	—4 ; —3
	2	22,012·8 ,,	22,461 .,	—4 ; —2
^1S	o	34,555·2 ,,	—	

* As the different 4*f*-electronic levels are due to different combinations of the ' l ' and ' s ' vectors of these electrons, it follows from general reasoning that here the inter-multiplet and the intra multiplet intervals will be the same function of the effective nuclear charge. It is because of this that the multiplication of all the intervals by the same constant factor is possible in this case.

It will be noticed in table V that the agreement between the calculated terms of Pr IV and the mean absorption frequencies of Pr^{+++} ions is fairly good. Besides this there are also other reasons in favour of the transitions assigned for the particular groups. Van Vleck showed that in the process of absorption by rare earth solids the strongest radiation will be quadrupole in nature allowing ΔL or $\Delta J = \pm 2$, ± 1 and 0. Further on account of the asymmetry, either present in the crystalline fields or brought about when the electron is set in vibration, transitions are possible where ΔL or ΔJ reaches a value up to ± 4. From the last column of the table it is apparent that these allowed changes are not exceeded in any case. Also the relative intensity of the absorption groups is found to be greater the lower the change occurring in the value of J, excepting the case $\Delta J = 0$, where weak radiation is expected. One point which is very significant is that in the above table no absorption group is specified for the transition $^3H_4 \longrightarrow {}^3F_4$. This may be due to the fact that on account of the low dispersion in the infra-red the corresponding relatively weak group was overlapped by the very strong group preceding it. This also accounts for the rather large interval between I and II which is found to be 1740 cm^{-1} while the calculated one is 1270 cm^{-1}. Gobrecht represented this transition by the weak group at 9835 cm^{-1}. But its interval from group II, which is $2{,}885 \text{ cm}^{-1}$, seems to be rather too high as compared with the calculated splitting, viz., $1{,}690 \text{ cm}^{-1}$.

In this preliminary classification it is not intended to deal with the origin of the fine structure shown in many of the groups. They could not be investigated in detail in some of the groups at the low temperature available in this laboratory. These have, however, been extensively investigated by Spedding and his co-workers [7] during the progress of the present work. From a study of the absorption spectra of many of the rare earth ions, Ellis [8] has proposed a scheme in which the successive excited inner states appear above their normal ground states. In Pr^{+++} they are respectively $^1I_6$, $^3P_{0,1,2}$. In the classification given above the successive excited states are represented by $^3F_{2,3,4}$; $^1G_4$; $^1I_6$; $^3P_0$, $I_{0,1,2}$. Although he has not yet published the complete account, it appears from a comparison of the two that he has perhaps taken into consideration only the absorption spectra in the visible region.

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PALIT PHYSICAL LABORATORY,
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        CALCUTTA.

STRUCTURE OF AROMATIC COMPOUNDS.
PART II. BENZIL

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ABSTRACT. The space group of benzil crystal has been found to be $D^4_3C3_12$ and $D^6_3C3_22$ for the two enantiomorphic forms. The molecular plane of each molecule is inclined to the triad axis at $13°$, the three molecules are parallel to the three basal axes and are arranged spirally about a three-fold screw-axis.

The chemical formula of benzil is very similar to dibenzil. The two hydrogen atoms attached to the two alipathic carbon atoms of the latter compound are replaced by one divalent oxygen atom. So it is expected that the carbon skeletons of these two compounds are practically the same, as the valency bonds that bind the carbon atoms are identical in these two compounds. Dibenzyl has been completely analysed by Dhar[1] by the trial and error method and by J. M. Robertson[2] by the Fourier Analysis Method. As the latter method gives more definite and accurate results, we may utilise, for the determination of the structure of benzil, the structure of the carbon skeleton of dibenzyl found by Robertson as our starting point. The similarity will be easily seen from the structural formulae given below :
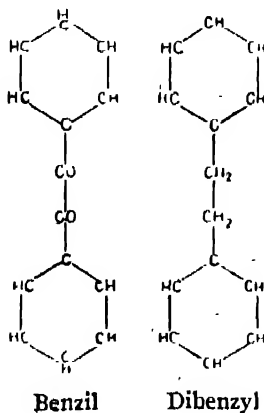

Benzil   Dibenzyl

FIGURE 1.

Benzil has been found by Des Cloizeauz (Groth's Chemische Krystallographie Vol. V., p. 200) to belong to the trigonal trapezohedral class with axial angle 78° 13′. Referred to the hexagonal system of axes, the axial ratio $a:c$ comes out 1:1.6322. The cell dimensions referred to the hexagonal system was determined by N. C. B. Allen[3] and found to be $a_0 = 8·15$ and $c_0 = 13·46$ with 3 molecules per unit cell.

The substance was crystallised from ether. Hexagonal prisms bounded by the six m ($2\,\bar1\,\bar1\,10$) faces were obtained. The end faces (001) were also developed in most of the crystals.

<center>DETERMINATION OF SPACE-GROUP.</center>

For determination of the space-group, the first point to be decided is whether the basic lattice is rhombohedral or hexagonal. When a rhombohedral lattice is referred to a hexagonal system of co-ordinates, it is converted into a body-centered hexagonal lattice, so that the number of molecules per unit cell becomes doubled. Thus if a crystal whose basic lattice is rhombohedral be referred to the hexagonal system the number of molecules per unit cell must be even. As this is not so in the case of benzil, the basic lattice cannot be rhombohedral.

From the rotation photograph about the 'c' axis all the spots could be identified unambiguously. The spots on the rotation photograph about 'a' axis could not be identified unequivocally and hence oscillation photographs of 10° range were taken. Due to the symmetry of the crystal only 9 photographs were necessary. For facilitating the identification in the oscillation photographs, the hexagonal lattice was transformed into an orthogonal one, by choosing the normal to a vertical axial plane as the second axis. The axial length in this direction is then 3 times that along the other basal axis. The reciprocal lattice can then be drawn in the same way as for orthogonal crystals, and after identifying the planes according to this system, the indices may be reconverted into the hexagonal system.

All the reflections observed with their estimated intensities are given in the table.

In the table of planes, we find that of all the 000l reflection only 0003, 0006, 000(12) appear while the other reflections are absent, i.e., reflections are absent whenever l is not divisible by 3. This shows that 'c' axis is a three-fold screw axis, and therefore the space-group is $D^4_3\ C3_1\,2$ or its enantiomorphic form $D^4_3\ C3_2 2$, the former rotating the plane of polarisation to the right and the latter to the left.

As the crystal possesses a three-fold screw axis the three-molecules of the unit cell must be placed at the three equivalent positions obtained by the screw axis. The crystal possesses in addition dyad axes, and hence each molecule must possess a two-fold axis, parallel to a basal axis,

LIST OF REFLECTING PLANES FOR BENZIL (OSCILLA-
TION ABOUT 'a' AXIS)·

Axial Planes :—

Plane.	Intensity.	Plane.	Intensity.
...	...	$01\bar{1}0$	M.
0003	S.	$02\bar{2}0$	S.
0006	M. S	$04\bar{4}0$	M. S.
000(12)	V. V. W.	$08\bar{8}0$	W.

Prism Planes :—

Plane.	Intensity.	Plane.	Intensity.
$01\bar{1}1$	W.	$02\bar{2}(10)$	M.
$01\bar{1}2$	V. S.	$02\bar{2}(11)$	M.W.
$01\bar{1}3$	S.	$02\bar{2}(12)$	M.W.
$01\bar{1}4$	S.	$03\bar{3}1$	M.S.
$01\bar{1}5$	S.	$03\bar{3}2$	S.
$01\bar{1}6$	M. S.	$03\bar{3}3$	S.
$01\bar{1}7$	M.	$03\bar{3}4$	S.
$01\bar{1}8$	V.V.W.	$03\bar{3}5$	S.
$01\bar{1}9$	M.	$03\bar{3}6$	M.S.
$01\bar{1}(10)$	W.	0337	M.
$01\bar{1}(13)$	V V.W.	$03\bar{3}8$	M.
$02\bar{2}1$	S.	$03\bar{3}(10)$	M.
$02\bar{2}2$	S.	$04\bar{4}3$	M.S.
$02\bar{2}3$	W.	0444	V.W.
$02\bar{2}4$	S.	$04\bar{4}6$	W.
$02\bar{2}5$	M.S,	$04\bar{4}7$	M.S.
$02\bar{2}6$	W.	$04\bar{4}8$	V.W.
$02\bar{2}7$	M.W.	$04\bar{4}9$	M.
$02\bar{2}8$	V.S.	$14\bar{4}(10)$	M.W.
$02\bar{2}9$	W.	$05\bar{5}2$	W.

Prism planes (contd.).

Plane.	Intensity.	Plane.	Intensity.
05$\bar{5}$4	S.	06$\bar{6}$ (10)	M.W.
05$\bar{5}$5	V.V.W.	07$\bar{7}$1	V.V W.
05$\bar{5}$7	M.S.	07$\bar{7}$4	V.W.
05$\bar{5}$9	M.W.	07$\bar{7}$5	M.
05$\bar{5}$ (11)	V.W.	07$\bar{7}$6	M.S.
05$\bar{5}$ (12)	V.W.	08$\bar{8}$4	W.
06$\bar{6}$2	M.S.	11$\bar{2}$0	S.
06$\bar{6}$3	V.V.W.	12$\bar{3}$0	S.
06$\bar{6}$4	W.	13$\bar{4}$0	M.S.
06$\bar{6}$5	M.W.	22$\bar{4}$0	S.
06$\bar{6}$7	M.W.	31$\bar{4}$0	M.S.

General planes.

Plane.	Intensity.	Plane.	Intensity.
11$\bar{2}$1	S.	12$\bar{3}$4	M.S.
11$\bar{2}$2	S.	12$\bar{3}$5	M.S.
11$\bar{2}$3	V.S.	12$\bar{3}$6	S.
11$\bar{2}$4	S.	12$\bar{3}$7	M.W
11$\bar{2}$5	S.	12$\bar{3}$8	M.W.
11$\bar{2}$6	S	12$\bar{3}$9	M.
11$\bar{2}$7	V.S.	12$\bar{3}$ (10)	M.
11$\bar{2}$8	M.	12$\bar{3}$ (12)	M,
11$\bar{2}$9	M.	13$\bar{4}$1	M,
11$\bar{2}$ (10)	M.W.	13$\bar{4}$2	S.
11$\bar{2}$ (11)	M.W.	13$\bar{4}$3	M.
11$\bar{2}$ (12)	W.	13$\bar{4}$4	M.
12$\bar{3}$1	S.	13$\bar{4}$5	S.
12$\bar{3}$2	M.	13$\bar{4}$6	S.
12$\bar{3}$3	V.S.	13$\bar{4}$8	M.S.

General planes (contd.).

Plane.	Intensity.	Plane.	Intensity.
1349	M.	2244	M.
$13\bar{4}$ (10)	V.V.W.	$224\bar{5}$	M.
$13\bar{4}$ (11)	W.	$224\bar{6}$	M.S.
$14\bar{5}1$	M.W.	$224\bar{7}$	M.S.
$14\bar{5}2$	M.	$224\bar{9}$	M.
1453	M.	$22\bar{4}$(10)	W.
$14\bar{5}4$	M.	$22\bar{4}$ (11)	V.W.
$14\bar{5}5$	M.	2351	M.
$14\bar{5}6$	M.	$23\bar{5}2$	M.S.
$14\bar{5}8$	V.V.W.	2353	M.S.
$14\bar{5}9$	M.	$23\bar{5}4$	M S.
$14\bar{5}$ (11)	V.W.	2355	M.
$15\bar{6}2$	M.S.	$23\bar{5}6$	S.
$15\bar{6}3$	M.S.	$23\bar{5}7$	M S.
$15\bar{6}4$	M.S.	$23\bar{5}8$	M S.
$15\bar{6}5$	M.S.	$23\bar{5}9$	W.
$15\bar{6}6$	M.W.	$23\bar{5}$ (10)	W
$14\bar{6}7$	M.W.	$23\bar{5}$ (11)	V.W.
$15\bar{6}8$	M.W.	$24\bar{6}2$	W.V.
$13\bar{6}9$	V.W.	$24\bar{6}3$	V.W.
$16\bar{7}3$	V.W.	2464	M S.
$16\bar{7}4$	W.	$24\bar{6}5$	M.W.
1675	M.W.	$24\bar{6}6$	M.W.
1676	M.W.	2467	M.
$16\bar{7}9$	M.W.	$24\bar{6}8$	M.
$17\bar{8}4$	V.W.	2469	M.W.
$17\bar{8}6$	M.	$24\bar{6}$ (10)	V.W.
$22\bar{4}1$	S.	$24\bar{6}$ (12)	V.W.
$22\bar{4}2$	M.S.	$25\bar{7}2$	V.V.W.
2243	M.S.	$25\bar{7}3$	V.W.

General planes (contd.).

Plane.	Intensity.	Plane.	Intensity.
$25\bar{7}4$	M.	$33\bar{6}4$	V.W.
$25\bar{7}5$	M.	$33\bar{6}5$	M.
$25\bar{7}6$	M.	3366	M.
$25\bar{7}8$	V.W.	$34\bar{7}1$	M.
$26\bar{8}6$	M.S.	3472	M.
$3\bar{1}47$	M.W.	3473	M.
$32\bar{5}$ (12)	M.W.	$34\bar{7}4$	V.W.
$33\bar{6}1$	M.W.	3475	M.
$33\bar{6}2$	M.	3476	M.W.
$33\bar{6}3$	M.	3477	V.W.

DETERMINATION OF THE ATOMIC ARRANGEMENT

We thus see that the benzil molecule has a two-fold axis of symmetry. From the chemical formula of benzil we find the two CH_2 groups must be derivable from each other through the axis of symmetry and so also the two benzene rings. This can happen only if this axis passes through the midpoint of the bond connecting the two CH_2 groups and is perpendicular to this bond. In dibenzil, it has been definitely found that the two benzene rings are parallel to each other, and as the carbon bonds are identical in these two cases and also from the symmetry of the bonds we conclude that there is no inclination between the two rings. So there are two possibilities. The two benzene rings may lie in the same plane or they may lie in parallel planes. In the case of dibenzil, it has been definitely proved by Robertson that the molecule is of the second type.

From analogy, we start with this structure for the benzil molecule and try to find its orientation in the crystal lattice. The mean gm. molecular susceptibility of benzil[4] is -110.4×10^6 e.m. units and is exactly double that of single benzene molecule whose mean gm. molecular susceptibility is -55.3×10^6 e.m. units. Hence we may consider that the components of molecular susceptibilities to be double of those for benzene so that

$$K_1 = K_2 = -74.6 \times 10^6 \text{ e.m. units.}$$

$$K_3 = -182.4 \times 10^6 \text{. e.m. units.}$$

Suppose that the molecular orientation is obtained by rotating it from the position in which the c-axis is parallel to the benzene rings through an angle θ, then since susceptibility along 'c' is—80×10^6 e.m. units, we have the relation

$$80 = 74.6 \cos^2\theta - 182.4 \sin^2\theta.$$

whence $\theta = 13^0$.

The atomic parameters as ratios of the axial lengths of the carbon atoms of half of a molecule are given in the following table. Those for the other atoms can be easily obtained by the operations of the dyad axis as well as the triad screw axis possessed by the unit cell.

Atomic parameters of benzil

Atoms	x	y	z
C_1	·061	·122	·006
C_2	·087	·174	·III
C_3	·269	·200	·161
C_4	·294	·251	·261
C_5	·138	·276	·312
C_6	—·042	·251	·261
C_7	·069	·200	·161

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ON THE RAMAN SPECTRA OF MIXED CRYSTALS.*

By S. C. SIRKAR

AND

ISHWARCHANDRA BISHUI.

PLATE XVI

ABSTRACT. The Raman spectra of mixed crystals of p-dichlorobenzene and p-dibromobenzene have been re-investigated. It is pointed out that the observed facts, which are at variance with some of those observed by Vuks, do not definitely lead to the conclusion that the new intense Raman lines having values of $\Delta\nu$ less than 100 cm^{-1} observed in these cases are due to lattice oscillations. It is pointed out that besides these investigations of the Raman spectra, investigations of other properties of the crystals have to be made before coming to the conclusion mentioned above.

INTRODUCTION.

The Raman spectra of crystals of p-dichloro- and dibromobenzene were first studied by Vuks[1] who concluded that there are two different modifications of the crystals of p-dichlorobenzene and from the fact that the new Raman lines observed in the neighbourhood of the Rayleigh line undergo changes with the change from one modification to the other, he also came to the conclusion that these new lines are due to lattice oscillations. These investigations were subsequently repeated by Sirkar and Gupta[2] who observed that when the crystals of p-dichlorobenzene are once cooled below 20°C and again allowed to attain the room temperature, besides some of the new lines close to the Rayleigh line, also the lines 305 cm^{-1} and 331 cm^{-1} due to intramolecular oscillations are slightly shifted. No such changes, are, however, observed in the case of p-dibromobenzene even when it is cooled in liquid ammonia, though according to Bech and Ebbinghaus[3], who studied this transformation in a number of substances, p-dibromobenzene should also exhibit two modifications, one above and the other below 8°C. Vuks next reported[4] the results of similar detailed investigation of the Raman spectra of these substances and he also observed the shifts of the lines 305 and 331 cm^{-1} mentioned above, besides those of the lines in the low frequency region and of

* Read before the meeting of the Indian Physical Society on 17. 12. 37.

few others of higher frequencies. He also observed that p-dibromobenzene exhibits only one crystalline structure at different temperatures. In order to interpret the results obtained by him more satisfactorily, he recently investigated[5] the Raman spectra of mixed crystals of these two substances. He observed that though the Raman lines due to intramolecular vibrations observed in the case of the mixed crystals are the same as would be obtained by mere superposition the Raman spectra of the two pure substances, the new lines close to the Rayleigh lines have positions intermediate between those obtained by such a superposition. He also observed that some of these new lines move closer to the Rayleigh line with the increase of percentage of p-dibromobenzene in the mixed crystal. Since similar results are obtained in the case of the "reststrahlen" frequency of mixed crystals of KCl and NaCl, he concluded that these new lines are due to lattice oscillations.

There is, however, a little difficulty in understanding some of the results reported by Vuks even if it be assumed that these new lines close to the Rayleigh line are due to lattice oscillations. As has been discussed by one of the present authors (S. C. S.) in a previous paper[6], it is difficult to understand why the intensity of the Raman line due to lattice oscillation observed in the case of centrosymmetrical molecule is many times larger than that of the line due to the symmetric breathing vibration of the molecule. Again, the shift of the lines 309 cm^{-1} and 330·5 cm^{-1} with the increase of percentage of p-C$_6$H$_4$Br$_2$ in the mixed crystals from 22% to 47% observed by Vuks cannot be easily understood because, these lines being due to intramolecular oscillations, their frequencies should depend only very slightly on the crystalline field and not on the relative percentages of the two substances in the mixed crystal. In order to understand these facts more clearly, the Raman spectra of these mixed crystals as well as of the pure substances in the solid and liquid states have been carefully re-investigated and the results have been discussed in the present paper.

EXPERIMENTAL.

Mixed crystals of p-dichloro and dibromobenzene of a few different compositions were prepared by melting in each case the requisite proportions of the two substances in a pyrex tube and allowing the melt to cool down slowly. In the case of mixtures with small percentages of p-dibromobenzene, large transparent crystalline masses were obtained on solidification. In the case of mixtures containing more than 40% of p-dibromobenzene, however, no such transparent mass was obtained but on keeping the tube containing the melt slightly inclined to the horizontal, the whole mass was attached to one side of the walls and small single crystals, the biggest having faces about 5 to 9 sq. mm. in area, were found to be

imbedded in the whole mass. In order to examine whether the composition in these single crystals was different from that in the surrounding translucent mass, one of these crystals was first used for studying the Raman spectrum and next some portion of the translucent mass was used. The ratio of the intensity of the line 1066 cm^{-1} of p-dibromobenzene to that of the line 1104 cm^{-1} of p-dichloro benzene was found to be almost the same in the two cases. It appeared, therefore, that the composition was nearly the same in the two cases.

Vuks, however, reported that the composition varies from point to point in the mixed crystal. He came to this conclusion by determining the melting point of samples taken from different portions of the mixed crystal. In order to ascertain the extent of variation of composition, the melting point of different samples taken from different portions of a solid solution containing equal masses of the two substances was determined. About 0·5 c.c. was taken each time. It was found that the melting point was not sharp, but the range was narrower in the case of the sample taken from the top portion than that in the case of the sample taken from the bottom. Melting started at 58°C in the former case and the temperature rose to 60°C till the whole mass taken completely melted. In the latter case, these two temperatures were found to be 59°C and 66°C, respectively. This fact shows that the composition is different in the two cases but the variation is not large at places sufficiently close to each other. In the actual investigation, the lower portions of the solid masses obtained by allowing the melts to cool down in pyrex tubes were used for studying the Raman spectra.

The Fuess spectrograph used in the present investigation produces no coma on the Stokes side of Hg 4047Å and has a dispersion of about 11·5Å/mm in this region. This dispersion is comparable to the dispersion 11Å/mm of the spectrograph used by Vuks in the investigations mentioned above. An attempt was made to improve the quality of the image still further by diminishing the aperture of the collimating lens of the spectrograph. Though the quality improved a little the Rayleigh line was always found to be overexposed owing to the extraneous light produced by reflections inside the crystalline mass and consequently there was blackening due to photographic spreading of the Rayleigh line up to about 25 cm^{-1} on each side from the centre of the line. Complementary light filters were tried to overcome this difficulty partially. As usual, a solution of iodine in carbon-tetrachloride was used in the path of the incident beam, but the other complementary filter placed in the path of the scattered light was an aqueous solution of samarium chloride* of suitable concentration. This filter has a strong absorption band at about 4038 Å and the edge of this band on the long wave-length side is sharp and may be brought to the region 4047 Å by adjusting the

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* The authors are indebted to Dr. P. B. Sarkar of the Chemistry Department for kindly lending about 2 gms. of SmCl$_3$.

concentration and the thickness of the cell. When this is done, the filter transmits freely the region 4049 Å – 4070 Å. This filter is therefore particularly suitable for studying the Raman lines having small frequency shifts. Inspite of using this filter and the spectrograph mentioned above, the line 20 cm^{-1} of solid p-dibromobenzene reported by Vuks could not be resolved from the Rayleigh line, though in the spectrograms reproduced by him, this line seems to be well separated from the Rayleigh line.

The Raman-spectra of p-dibromo and dichlorobenzene in the liquid state were also photographed with the same spectrograph in order to ascertain whether any of the Raman lines shift from their original positions on solidification of the melt. The tubes containing the substances were kept heated above the melting points by keeping them inside a cylindrical electrical heater which was provided with suitable windows. A condenser was used to illuminate the substances by focussing the light from a mercury arc. Ilford Special Rapid plates were found to be suitable for studying the Raman spectra of solids. Iron arc spectrum was photographed on each plate and used as a comparison for the measurement of wave-lengths. It was possible to measure the frequencies of Raman lines correct at least to 1 cm.$^{-1}$

TABLE I.

Composition (%).		Temperature in °C	$\Delta \nu$ of Raman lines in cm^{-1}		
$C_6H_4Cl_2$	$C_6H_4Br_2$				
100	0	31	40 (2s) 50 (2s)		82 (2b)
100	0	,, (after being cooled in ice)	48 (2)		93 (2b)
82	18	31	47 (2)		93 (3b)
72	28	,,	47 (2)		93 (3b)
50	50	,,	36(?) 47 (2)		93 (4b)
40	60	,,	36 (1) 47 (2)		93 (4b)
0	100	,,	36 (3s)		93 (2b)

RESULTS AND DISCUSSION.

The Raman lines having small frequency-shifts observed in the case of the solid substances and mixed crystals are tabulated in table I. The positions of some of the lines having values of $\Delta \nu$ greater than 200 cm^{-1} observed in the .se of the substances under different conditions are shown in table II. Some
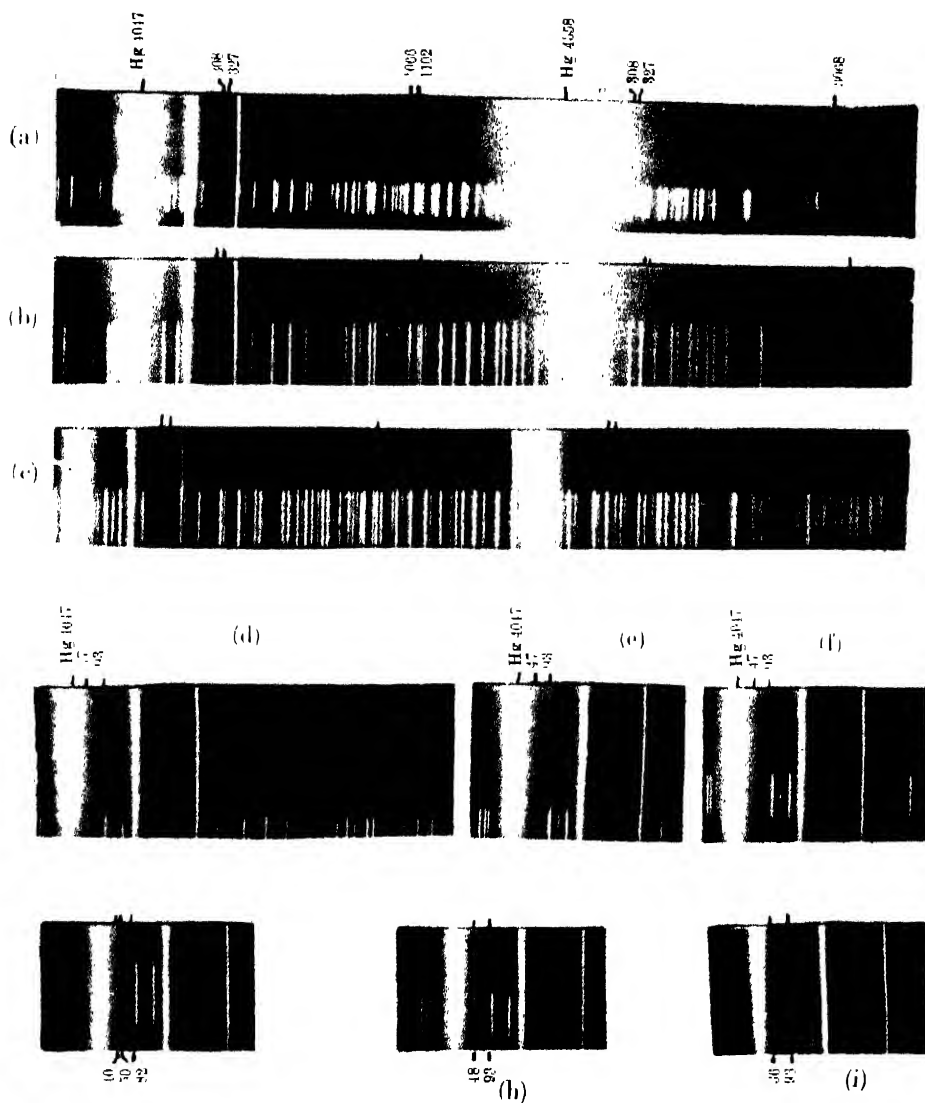
Raman Spectra

(a) 82% $C_6H_4Cl_2$ + 18% $C_6H_4Br_2$
(b) $C_6H_4Cl_2$ (β-modif.)
(c)   ,,   liquid
(d) 50% $C_6H_4Cl_2$ + 50% $C_6H_4Br_2$
(e) 72%   ,,   + 28%   ,,
(f) 82% $C_6H_4Cl_2$ + 18% $C_6H_4Br_2$
(g) $C_6H_4Cl_2$ (α-mod.)
(h)   ,,   (β-mod.)
(i) $C_6H_4Br_2$ (cryst)

TABLE II.

Substance	State.	Temp in °C	Δν of prominent Raman lines in cm⁻¹.
$C_6H_4Cl_2$	liquid	80	300(2) 330(3) 745(4) 1100(5) 3072(5b)
,,	solid	31 (β-mod)	305(1) 330(2) 745(3) 1102(4) 3070(4)
,,	,,	,, (once cooled in ice, α-modif.)	308(1) 327(1) 745(2) 1102(3) 3070(3)
82% $C_6H_4Cl_2$ + 18% $C_6H_4Br_2$	,,	31	308(1) 327(1) 745(2) 1102(3) 3068(3)
50% ,, + 50% ,,	,,	,,	308(1) 327(1) 745(2) 1102(3) 3067(3)

of these spectrograms have been reproduced in plate XVI, but it has to be pointed out that owing to the proximity of the very intense Rayleigh line, the Raman lines having small values of Δν could not be reproduced well although in the original spectrograms they were fairly intense. Incidentally it may be pointed out that the reproductions of the spectrograms in plate I of one of the papers by Vuks [4] are not reliable because the relative intensities of the lines are anomalous. As for instance, the lines 27 cm⁻¹ and 50 cm⁻¹ excited by Hg 4077Å are more intense than the lines 305 cm⁻¹ and 327 cm⁻¹ in spectrogram *c*, but in *d* the former two lines are totally absent although the latter two lines are fairly intense. Again, in spectrogram *d*, the line 327 cm⁻¹ is almost as intense as the Hg line 4108Å but even in the liquid state, in which stray light is eliminated, the ratio of the intensities of the two lines is about 1:10.

The results reported by Vuks are given in tables III and IV.

TABLE III (Results reported by Vuks).

Composition.		Melting point. (°C.)	Δν of lattice frequencies in cm⁻¹		
% $C_6H_4Br_2$ mol.	% p-$C_6H_4Cl_2$ mol.		ω_1	ω_2	ω_2
100	0	86·7	20·1	37·8	93
78	22	82·3	20·2	39·5	93
47	53	69·0	22	42·1	94
22	78	60·5	24	46·3	94
9	91	56	26·2	50	93
0	100	53·0	27·5	$\begin{cases} 46·5 \\ 54·0 \end{cases}$	93

TABLE IV (Results reported by Vuks).

Substance	State.	$\Delta \nu$ of prominent Raman lines in cm^{-1}				
$p\text{-}C_6H_4Cl_2$	Liquid	299·7 (5)	329·5 (10)	748·1 (10)	1108·4 (10)	3071·3 (10)
,,	Solid (β-modification)	304·1 (5)	329·5 (10)	745·2 (10)	1103·9 (10)	3072·2 (10)
,,	Solid (α-modification.)	307·6 (5)	328·0 (10)	745·0 (10)	1104·5 (10)	3071·3 (10)
78% $C_6H_4Cl_2$ + 22% $C_6H_4Br_2$	Solid	309	330·5	..	...	...
53% $C_6H_4Cl_2$ + 47% $C_6H_4Br_2$.	,,	307·4	327·5	...	...	...

It will be seen by comparing the results obtained in the present investigation with those reported by Vuks that there is disagreement between these two sets of results in various respects.

First, according to Vuks, frequencies ω_1 and ω_2 shown in table III diminish with the increase of percentage of $p\text{-}C_6H_4Br_2$ in the mixed crystal. On the other hand it has been observed in the present investigation that ω_2 remains in the same position for all the compositions studied. With the help of iron arc spectrum as comparison this fact was definitely ascertained. Secondly, there is disagreement between the results given in table II and those observed by Vuks and reproduced in table IV. The lines 308 cm^{-1} and 327 cm^{-1} remain in the same position for different composition of the mixed crystal, as can be observed from table II but Vuks reported that the positions shift with the change of the composition. Thirdly, the absolute values of $\Delta \nu$ observed by Vuks do not agree in all the cases with those observed by the present authors. As has already been mentioned, care was taken to determine these values with the help of iron arc spectrum as comparison. Vuks has not mentioned whether this method was employed by him also, but he has given his results in such a way that it appears as if the results are correct to 0·1 cm^{-1}. It is needless to point out, however, that with the spectrograph used by him such an accuracy cannot be attained.

The position of the lines in the low frequency region are the same in the case of the mixed crystals containing 18% of p-dibromobenzene as in the case of α-modification of p-dichlorobenzene. This fact has also been observed by Vuks who has observed that the α-modification is obtained by mixing even 1% to 2% of p-dibromobenzene with p-dichlorobenzene. From this he has concluded that p-dibromobenzene is isomorphic with the α-modification and not with the β-modification of p-dichlorobenzene. The crystal structure of these two substances as well as of their solid solutions has been studied by Hendricks.[7] The projection

of the unit cell on the *a c* plane is shown in figure 1. In the case of *p*-dichloro-benzene, the molecules are almost parallel to the *a* axis as shown in figure 1(*b*), but in the case of *p*-dibromobenzene they are inclined to this axis as shown in figure 1(*a*). The dimensions of the unit cell are almost identical in the two cases. It has been observed by Sirkar and Gupta[8] that the crystal lattice remains the same when $\beta \longrightarrow \alpha$ transformation takes place. The only other change in the structure which may take place during this transformation is the rotation of the molecules from the positions

(a)   (b)
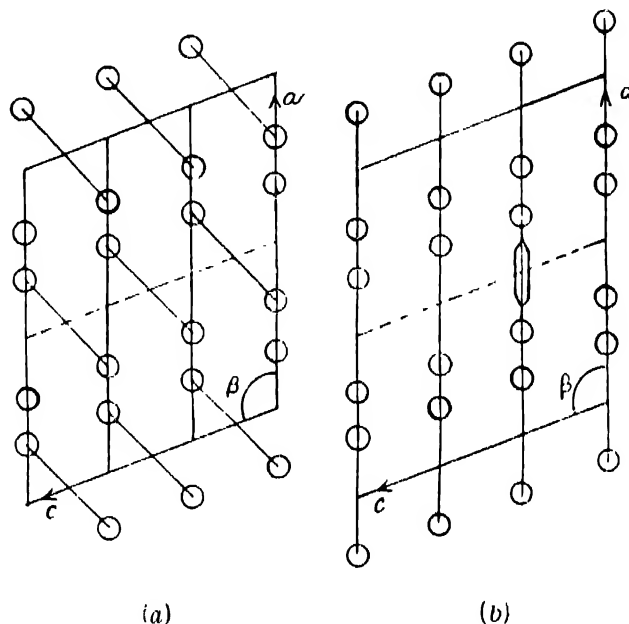
FIGURE 1.

shown in figure 1(*b*) to those in figure 1(*a*). With such a change, however, there are associated large changes in the relative intensities of X-ray reflections from various planes and such changes have not been observed in the intensities of the Laue spots by Sirkar and Gupta. With such a change in the structure, no change in volume takes place, and according to Vuks the transformation from $\alpha \longrightarrow \beta$ modification takes place without any change of volume and is therefore connect-ed with the rotation of the molecules from one position to the other. According to this hypothesis, the structure of α-modification of *p*-dichlorobenzene would be the same as that of *p*-dibromobenzene shown in figure 1 (*a*) The mixed crystal containing a very small percentage of *p*-dibromobenzene, on this hypothesis. would also have the same structure as that of *p*-dibromobenzene and not of *p*-dichlorobenzene, though on the contrary it may be expected that a few molecules of *p*-dibromobenzene, when mixed with a large number of molecules of *p*-dichlorobenzene, should not alter the orientation of the latter molecules in the unit cell but should be accommodated in the origi-

nal lattice of the latter. Hendricks[9] has shown that the structure of equimolal solid solution of the two substances is the same as that of p-bromochlorobenzene, and this latter substance again has the same structure as p-dibromobenzene, but he has not mentioned whether the structure is the same in solutions of all compositions, and probably it is not so. Again, Vuks finds from the composition $-\Delta\nu$ curve that the positions of the lines in the low frequency region observed in the case of p-bromochlorobenzene are the same as those in the mixed crystals containing 47% of p-dibromobenzene, and in the equimolal solid solutions, these positions are slightly different from those in p-bromochlorobenzene. These results do not agree with those obtained by X-ray analysis mentioned above.

The values of $\Delta\nu$ which are observed for the lines 300 cm^{-1} and 330 cm^{-1} in the case of the mixed crystals are 308 cm^{-1} and 327 cm^{-1} respectively for the different compositions and the values 309·0 cm^{-1} and 330·5 cm^{-1} for the composition 22% p-$C_6H_4Br_2$ + 78% p-$C_6H_4Cl_2$ given by Vuks are not correct. Vuks has pointed out that the position of these lines shift with the change of composition in the mixed crystals but it has been found in the present investigation that they do not do so. It can be clearly seen from the spectrograms reproduced in plate XVI that in the case of the mixed crystals containing only 18% by weight of p-$C_6H_4Br_2$, the value of one of the lines is much less than the value 330·5 cm^{-1} given by Vuks. Again, it has been found that the line 745 cm^{-1} remains in the same position in all the states but according to Vuks the position of this line would shift a little on solidification of the melt. The shift of the hydrogen line 3072 cm^{-1} with the increase of percentage of p-$C_6H_4Br_2$ in the mixed crystals is probably due to the fact that the value of $\Delta\nu$ for pure p-$C_6H_4Br_2$ is slightly less than that for pure p-$C_6H_4Cl_2$.

The above facts, therefore, do not suggest that there is any definite relation between the composition of the mixed crystals and the positions of the new lines and it cannot be definitely concluded from these facts that the lines in the low frequency region are due to lattice oscillations. It can be ascertained, however, by studying the other properties of these crystals, as for instance, optical double refraction, whether there is any change in the orientation of the molecules in the unit cell with the transformation from one modification to the other. The observed difference between the Raman spectra can be explained, on the other hand, without assuming such a change in the orientation of the molecules. There may be some weak electronic binding between different molecules, the corresponding states being quantised, and there may be two such states close to each other such that the transformation from one state to the other is possible either with the change of temperature or with the addition of a small quantity of impurity. It must be admitted, however, that before coming to such a definite conclusion, one has to prove by investigations more exhaustive than hitherto made that there is no change in the

orientation of the molecules in the unit cell of *p*-dichlorobenzene with the addition of a small percentage of *p*-dibromobenzene in the crystal or with the change of temperature. These investigations will be undertaken as soon as opportunity permits.

The authors are indebted to Prof. D. M. Bose for providing all the facilities for carrying out the investigation in his laboratory and also for allowing one of the authors (I. C. B.) to work in collaboration with the other author.

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9

NUCLEAR STRUCTURE OF LIGHT ATOMS

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ABSTRACT. It has been suggested in the following paper that the nucleus may be regarded as a kind of crystalline structure rather than an ensemble of protons and neutrons, as a static or at any rate a quasi-static system, rather than dynamical. The principles and methods of Quantum Mechanics have not, therefore, been applied. Born's unitary theory gives a field which differs only slightly from the Coulomb field, which may be supposed to be playing an important role in the nuclear structure. On this hypothesis, it has been shown that the ratio between two fundamental distances in the assumed structure for α-particles lies between two narrow limits. Calculations from mass-defects give the distance between elementary particles of the nucleus as of order 10^{-14} cms., the figure generally accepted. The structure of the isotopes of hydrogen, helium and lithium has also been considered. Since the identity of the different elementary particles of the nucleus of the same isotope is denied, the difficulty about the continuous energy-spectrum of β-radiation seems to admit of a simple solution.

Modern views on the nuclear structure regard the ultimate constituents as neutrons and protons which are supposed to form an ensemble obeying the Bose-Einstein or Fermi Dirac statistics according as the number of the constituent particles are even or odd. The interaction forces, according to Majorana [1] are of the Exchange type, which seeks to explain the high binding energy of the helium nucleus as compared with the deuteron. It is held that this hypothesis clears, to a certain extent, the difficulties which were experienced about the spin. It is an odd multiple of $\frac{1}{2}h'$, if the number of particles is odd, and even, if the number of particle is even. This simple rule encountered its first exception in nitrogen on the older electron-proton hypothesis. But the newer neutron-proton hypothesis overcomes this difficulty. There remains again the standing difficulty of the continuous energy spectrum of the β-radiation, which has been explained by Fermi on the assumption of a new elementary particle, the neutrino which though incapable of observation, is considered necessary if the Principle of Conservation of Energy is to be saved.

Among the objections to the scheme may be put forward the following considerations. The two systems of statistics are based on entirely different assumptions about the behaviour of the component particles. The Bose-Einstein statistics presuppose an entire absence of interaction so that any number of particles can occupy the same cell of the generalised position and momentum

space, while in the Fermi-Dirac system, the interaction is so strong that not more than one member can occupy one such cell. It is difficult to see why the addition of a single particle should make such a great difference in the behaviour of the constituent particles.

Regarding Majorana exchange forces, Tamm and Ivanenko [2] have calculated that on the assumption of Fermi's expression, the distance between each pair of protons and neutrons must be of order, 10^{-17} or less, before they can be effective. This is certainly very small compared with the accepted figures for the radii of the nuclei or of the ultimate particles.

Thirdly, by the replacement of electrons and protons as ultimate particles neutrons and protons does not really solve the difficulty about the spin momentum, but merely puts it back one place. It has been found that neutrons, protons and electrons all possess spin momentum of $\frac{1}{2}h'$, so the same difficulty re-appears in the case of the neutrons, which are regarded as built up of protons and electrons in some way or other. The principle of conservation of angular momentum cannot be salvaged if only algebraic addition is allowed.

The main idea of the present paper is to consider the nucleus as a sort of crystalline structure in which the complex nuclei are built out of the simpler materials. The ultimate particles are assumed to be protons and electrons.

In the first place, this meets the difficulty about the spin of the neutron. The idea of a crystalline structure implies vector addition of spin, and it is only by vector addition that $\frac{1}{2}h'$ added to $\frac{1}{2}h'$ can give $\frac{1}{2}h'$. Born [3] has formulated a unitary field theory in which matter has been sought to be blended with the electro-magnetic field. It is a consequence of that theory that the Potential

Function due to a charge c at distance r is expressed as $\phi(r) = \dfrac{c}{r_0} f\left(\dfrac{r}{r_0}\right)$ where

$f(x) = \displaystyle\int_x^\infty \dfrac{dx}{\sqrt{1+x^4}}$ where $x = r/r_0$, r_0 being a standard length. If we tabulate the values of $f(x)$ for different values of x we find that the law does not differ materially from the Coulomb Law when $r/r_0 > 1$.

TABLE I.

x	$f(x)$	$xf(x)$
1	0·927	·927
1·11	0·854	·948
1·25	0·792	·965
1·43	0·685	·980
1·67	0·592	·989
2	0·499	·994
2·50	0·399	·998
3·33	0·300	·999
5	0·200	1
10	0·1	1

It may be mentioned here that Born's value for r_0, "radius of the electron" is 2.28×10^{-13} cm. which probably is higher than what would be acceptable in the light of modern experimental facts.

For simplicity, in the following pages, the law of forces has been taken as that of Coulomb which plays the most important role. Besides, there would be other forces at work, *e.g.*, those due to magnetic moments, whose nature is but imperfectly known. But from the known energies of β-particles, which range up to 12×10^6 electron Volts, it seems reasonable to assume that these forces have a very low potential compared to the Coulomb potential. For, it is generally accepted that the linear dimensions of the complex nuclei are of order 10^{-12} cms. The distances between contiguous particles must therefore be of order 10^{-14} at most. At this distance, the Coulomb potential energy of an electron in the nucleus may be taken as of order $\lambda e^2/r$ where λ is an arithmetical constant of order 1, and r, the distance from the nearest particles, which is sufficient to account for the energy of order 23×10^{-6} ergs or 13×10^6 electron Volts.

Taking the simplest case of the deuteron, $_1H^2$, we may suppose it to be made up of one electron and two protons, one on each side, at distance a from the former. The mass defect is known to be 2.25×10^6 ev $= 3.6 \times 10^{-6}$ ergs If therefore, we consider Coulomb Potentials only,

$$\frac{3}{2} \frac{e^2}{a} = 3.6 \times 10^{-6} \text{ which gives } a = 9.6 \times 10^{-14}.$$

Similarly $_2He^3$ may be regarded as being made up of one electron and 3 protons symmetrically arranged in the three corners of an equilateral triangle with the former at the centroid. If a be the distance of the electron from each of the protons, it is easily verified that the latter are prevented from flying away by the Coulomb forces. The mass defect of the nucleus is known to be 7.2×10^{-3} M. U. $= 106.6 \times 10^{-7}$ ergs. The Coulomb potential energy is easily calculated to be $1.27e^2/a$.

Equating the two, we get $a = 2.9 \times 10^{-14}$ cms.

But the most interesting case is that of the helium nucleus, $_2He^4$, which may be supposed to be made of 2 electrons and 4 protons placed symmetrically on the three axes of a rectangular Cartesian set. Each of the protons is at a distance a from the origin, while each of the electrons is at a distance d from the origin. We shall first show that considered as a statical system, the particles have no tendency to fly away.
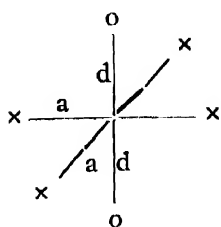
Let us calculate the force on one of the electrons represented by a circle directed towards the origin. This equals

$$e^2 \left\{ \frac{4d}{(a^2 + d^2)^{3/2}} - \frac{1}{4d^2} \right\}.$$

FIGURE I.

In order that this may be positive

$$16\, d^3 > (a^2 + d^2)^{3/2}$$

or, $$2^8\, d^6 > (a^2 + d^2)^3$$

or, $$4^3 \sqrt{4}\, d^2 > a^2 + d^2$$

or, $$5.4\, d^2 > a^2$$

or, $$d^2 > .18 a^2$$

or, $$d > .4a.$$

For a proton the force directed towards the origin is

$$e^2\left\{ \frac{2a}{(a^2 + d^2)^{3/2}} - \frac{1}{\sqrt{2}\, a^2} - \frac{1}{4a^2} \right\}.$$

In order that this may be positive

$$\frac{2a^3}{(a^2 + d^2)^{3/2}} > \frac{1}{4} + \frac{1}{\sqrt{2}}$$

or $$\frac{a^3}{(a^2 + d^2)^3} > .48$$

or $$a^2 > .61\,(a^2 + d^2)$$

or $$.39\, a^2 > .61\, d^2$$

or $$d^2 < \frac{.39}{.61}\, a^2$$

$$< .63\, a^2$$

or $$d < .8a.$$

Therefore, to prevent disintegration

$$.4a < d < .8a.$$

The Potential Energy of the system is

$$e^2\left\{ \frac{1}{2d} - \frac{8}{(a^2 + d^2)^{1/2}} + \frac{2}{2a} + \frac{4}{\sqrt{2}a} \right\}.$$

Taking $d = \cdot 5a$, this

$$= e^2 \left\{ \frac{2 + 2 \ \sqrt{2}}{a} \ - \ \frac{16}{\sqrt{5}a} \right\} \ = \ - \ 2 \cdot 30 \ e^2/a.$$

Since the mass-defect of an α-particle is $42 \cdot 3 \times 10^{-6}$ ergs, we have

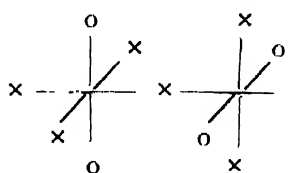$$2 \cdot 3 \times \frac{e^2}{a} = 42 \cdot 3 \times 10^{-6}$$

$$\therefore \qquad a = \frac{e^2 \times \cdot 23 \times 10^6}{423} = 1 \cdot 2 \times 10^{-14} \text{ cms.}$$

This gives approximately the accepted dimensions.

The question of spin has then to be considered. It must be pointed out here, that the generally accepted fact that the spin momentum of the elementary particles protons, electrons, positrons, neutrons (and even neutrinos) is $\frac{1}{2}h'$ leads apparently to insuperable difficulties. The term spin in Quantum Mechanics has not, of course, the same definite sense as it possesses in classical Mechanics. But if it has the magnitude given by its "eigenvalues," easy calculations show that the velocity at the periphery of the particle exceeds the velocity of light.

If this difficulty be brushed aside, the electrons and the protons in the above model must be supposed to have antiparallel spins, symmetrical with respect to the origin, to make the resultant spin of the α-particle zero.

Li has two isotopes $_3\text{Li}^7$ and $_3\text{Li}^6$ which occur in the proportion of 94:6. The following model may be suggested for the former, the crosses standing for the protons and the circles for the electrons. This indicates that $_3\text{Li}^7$ will break up easily into two α-particles if an additional proton be supplied—an experimental fact. In the absence of any knowledge of the magnetic forces, it is futile to attempt any definite theory about the direction of the spin, but

FIGURE 2.

obviously an odd multiple of the unit $\frac{1}{2}$ h' (1 or 3) is indicated by the presence of the three protons in a straight line while the spins of the pairs of protons and electrons may be supposed antiparallel and therefore neutralise one another.

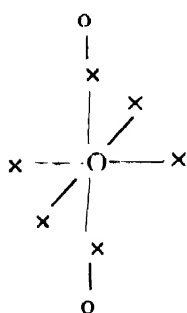For $_3\text{Li}^6$, the following model is suggested. The presence of two protons and an electron near the centre suggests the possibility of disintegration by shedding a neutron or a deuteron. β-disintegration has been a great stumbling block in the path of nuclear theories. Fermi's hypothesis of neutrinos invests them with residuary properties and places them at the same time, beyond possibilities of experimental verification— at least with our present resources. This is hardly satisfactory. It is obvious that some such hypothesis is necessary if the principle of conservation of energy is to be retained, provided the principle of identity of the different nuclei and the different elementary

FIGURE 3.

particles is assumed. But if it be assumed that the internal structure is crystalline, the electrons in the different positions will be at different energy levels. It is conceivable that two nuclei of the same isotope have different internal energy levels. The energy spectrum of β-radiation is then capable of a simple explanation.

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